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PROJECT PLAN

for the

VASQUEZ BOULEVARD & I-70 SITE
DENVER, CO

PILOT-SCALE
SOIL CHARACTERIZATION STUDY

September 9, 1999

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This Project Plan for the Vasquez Boulevard & I-70 Site – Pilot Scale Soil Characterization Study has been prepared at the request of the U.S. Environmental Protection Agency, Region 8, by ISSI Consulting Group, Inc. Study investigations and activities addressed in this Project Plan are approved without condition.

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TABLE OF ABBREVIATIONS

As	Arsenic
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CCOD	City and County of Denver
Cd	Cadmium
CDPHE	Colorado Department of Public Health and Environment
CEC	Cation Exchange Capacity
CLP	Contract Laboratory Program
COC	Chain of Custody
COPEEN	Colorado Peoples Environmental and Economic Network
CSM	Conceptual Site Model
CVAA	Cold Vapor Atomic Absorption
DMP	Data Management Plan
DQA	Data Quality Assessment
DQOs	Data Quality Objectives
GFAA	Graphite Furnace Atomic Absorption
GLP	Good Laboratory Practices
g	grams
H_o	Null Hypothesis
H_1	Alternative Hypothesis
Hg	Mercury
IATA	International Air Transport Association
ICP	Inductively Coupled Plasma
ID	Identification
IDW	Investigation Derived Waste
In	Indium
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MS	Mass Spectrometry
NIST	National Institute of Standards and Technology
oz	Ounces
PARCC	Precision, Accuracy, Representativeness, Completeness and Comparability
Pb	Lead
PE	Performance Evaluation
ppm	Parts per million
PQLs	Practical Quantitation Limits
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RPD	Relative Percent Difference
RPM	Remedial Project Manager
SDG	Sample Delivery Group
Sb	Antimony
Se	Selenium

SOPs	Standard Operating Procedures
SRM	Standard Reference Material
Tl	Thallium
TOC	Total Organic Carbon
USEPA	Unites States Environmental Protection Agency
VBI70	Vasquez Boulevard and Interstate 70
XRD	X-ray Diffraction
Zn	Zinc

1.0 Introduction

The U.S. Environmental Protection Agency (USEPA), Region 8 is working in cooperation with the Vasquez Boulevard and I-70 (VBI70) Working Group [City and County of Denver (CCOD), the Colorado Department of Public Health and Environment (CDPHE), the Agency for Toxic Substances and Disease Registry (ATSDR), the Colorado Peoples Environmental and Economic Network (COPEEN) and members of the public] to determine if residential soils and contamination in residential soils may be distinguished from source soils and other potential sources of contamination, using physical and chemical characteristics unique to each soil/material type. This Project Plan presents the organization, site background information, study objectives, laboratory analysis design and rationale, and specific quality assurance and quality control activities to support a pilot-scale soil characterization study.

1.1 Key Personnel

The following lists key personnel who will serve as contacts and provide technical expertise during implementation of this Project Plan.

U.S. Environmental Protection Agency

- Bonita Lavelle, USEPA Remedial Project Manager (RPM), will be responsible for overall project management, technical oversight and coordination among USEPA and its contractors, and the VBI70 Working Group. Ms. Lavelle will be a principal decision-maker for this project.

- Christopher P. Weis, Ph.D., USEPA Regional Toxicologist, will serve as the primary technical contact for this project. He will be responsible for technical oversight and evaluating the human health risk to residents of the Vasquez Boulevard and I-70 site. Dr. Weis will be a principal data user and decision-maker for this project.

1.2 Project Background

The VBI70 site is located in the northern section of Denver, Colorado. The study area is bounded on the west by the South Platte River and is approximately bounded on the east by Colorado Boulevard. Northern and southern boundaries for the study area are East 52nd Avenue and Martin Luther King Boulevard, respectively. A small area south of Globeville is also included. Its boundaries are: Interstate 70 on the north, West 39th Avenue on the south, Huron Street to the west, the South Platte River on the east and the Burlington Northern Railroad on the southeast.

Previous investigations begun in the vicinity of the Globe Smelter revealed the presence of residential soil contamination with metals associated with historic operations of the smelter. As sampling activities were extended further from the smelter, a number of

residential properties with higher than anticipated levels of metals (especially arsenic) in yard soil were identified. The discovery of these elevated soil levels in residential areas is the basis for establishing the VBI70 site. USEPA has conducted a number of studies in the area of the site to provide an initial characterization of the nature and extent of the contamination. Key findings and conclusions from these studies are summarized below:

- The chemicals of principal human health concern are arsenic and lead (ISSI 1999a).
- The spatial pattern of contaminated properties across neighborhoods appears to be unpredictable, with impacted yards occurring at widely separated locations, often surrounded by non-impacted properties (USEPA 1998a, 1998b, 1999a).
- Within a property that has elevated levels of arsenic, the pattern of contamination is generally widespread (covering most of the yard), but concentrations may vary significantly from place to place (USEPA 1999a). Figures 2.2.1-2.2.7 illustrate this pattern.
- Contamination is generally highest at the surface, diminishing at depths of 12-24 inches (USEPA 1999a, ISSI 1999b).
- The chemical form of the arsenic is mainly arsenic trioxide (USEPA 1998c).

Based on these data, USEPA has concluded that concentrations of arsenic and, to a lesser extent, lead in surface soil may be of health concern to some (but not all) area residents. Because of this concern, USEPA placed this site on the National Priorities List in April, 1999.

The source of the arsenic in the soil of impacted properties is not known. One hypothesis is that the main source is either atmospheric deposition of smelter emissions or importation of fill material from locations contaminated with smelter waste. An alternative hypothesis is that the arsenic is derived mainly from the application of arsenical-containing yard care products. Drexler (1998) performed geochemical speciation of arsenic in soils located in the vicinity of the Globe smelter. In general, Drexler found that arsenic trioxide was the dominant form in arsenic-contaminated contaminated soils. Based on an analysis of the relative content of other metals, Drexler concluded the source of the arsenic was predominantly pyrometallurgical. However, similar studies have not yet been performed on soils within the VBI70 site, and the source of the high arsenic levels seen in this area remain largely unanswered.

1.3 Project Description

The purpose of this study is to investigate whether the source of arsenic in residential soils can be identified by characterizing and comparing the physical and chemical characteristics of residential soils (and the contamination therein) and potential sources. Because no one measure is thought to be capable of distinguishing between the two candidate sources with certainty, the study design will employ a weight-of-evidence

approach in which a number of different physical and/or chemical characteristics of yard soils and candidate source materials will be measured. It is hoped that a diagnostic set of characteristics (a "fingerprint") may be identified that will allow a conclusion as to whether residential soils are more likely to be contaminated with smelter-related soils and materials or with an arsenical herbicide[1].

In order to test this method thoroughly prior to implementation, a pilot-scale investigation is initially proposed. A limited number of samples will be obtained from residential soils that have been archived as part of past sampling events. This will allow for evaluation of the diagnostic potential associated with this characterization approach while minimizing sampling and analysis costs. If the fingerprinting method proves sufficiently diagnostic, then a larger investigation that includes a field sampling effort may be developed. In that event, a separate project plan will be developed.

1.3.1 General Study Objectives

This project plan consists of three primary goals, which are provided below. These goals are focused upon obtaining information about the diagnostic characteristics (or "fingerprint") of the proposed analytical methods for distinguishing between soils/materials.

> General Objective #1: Develop a "fingerprint" for physical and chemical attributes associated with residential soils (and contamination therein), on-smelter facility soils/materials, and an arsenical herbicide (PAX) by applying a series of analytical methods to determine specific characteristics for each particular type of material.
>
> This will be accomplished by completing specific (individual) goals, which are:
>
> - Measure bulk soil characteristics such as pH, color, cation exchange capacity (CEC), mineralogy, sand/silt/clay, etc. for each soil (see Table 2.5.1 for complete list of analyses);
> - Measure chemical characteristics such as metals concentrations (see Table 2.6.1 for complete list of analytes), sulfate and chloride concentrations, isotope ratios for lead, geochemical speciation and *in vitro* bioaccessibility for each soil or material type;
> - Measure the frequency of occurrence of perlite present in each soil or material type; and
> - Combine physical and chemical results for each material type creating a "fingerprint" that represents the characteristics for each material.

[1] USEPA Region 8 has received information that an herbicide called PAX was commercially available in the 1950s to 1970s. This herbicide is reported to contain arsenic trioxide, lead arsenate, perlite, ammonium sulfate and silica sand (under USEPA 104(e) authority).

General Objective #2: Compare the "fingerprint" that specifically characterizes each type of soil or material to determine if the fingerprint characterization may distinguish residential soils (and contamination therein) from potential source area soils and materials.

This will be accomplished by completing specific (individual) goals, which are:

- Compare the "fingerprint" developed for each soil or material and determine whether a particular source may be attributed to arsenic and lead levels, as well as to the types of arsenic or lead found in residential soils;

- Perform a qualitative comparison of the "fingerprint" (physical and chemical parameters) between each type of soil or material and using professional judgement, determine whether patterns, trends or differences between materials exist.

2.0 Study Design and Implementation

Soil characterization will likely rely on a combination of chemical and physical characteristics of a soil or material, therefore a weight-of-evidence approach to soil characterization will be employed. It is important to obtain and evaluate all data prescribed herein, in order to meet the study objectives and to evaluate data on a weight-of-evidence basis. Several types of information are necessary. A matrix that summarizes the data planned for collection is provided in Table 2.0.1. Each of these analyses is described in detail in subsequent sections.

Table 2.0.1– Physical and Chemical Analyses by Sample Type

Sample Type	Physical Analyses		Chemical Analyses			
	Bulk Soil Characteristics	Electron Microscopy (perlite frequency)	*In Vitro* Bioaccessibility of Arsenic and Lead	Metal Conc.	Arsenic and Lead Speciation and Phase ID	Lead Stable Isotope Ratios
Residential Soil – High Arsenic	X	X	X	X	X	X
Residential Soil- Intermediate Arsenic	X	X	X	X	X	X
Residential Soil – Low Arsenic	X	X	X	X	X	X
On-Smelter – High Arsenic	X	X	X	X	X	X
PAX	--	X	X	X	X	X

-- Not Applicable
ID - Identification

The results for each of these analyses will be used to develop a "fingerprint" for each type of material. The "fingerprints" for each type of soil or material will be compared with other soils and/or materials to determine if they are similar or dissimilar. Specific details of these comparisons are provided in Sections 2.5.1, 2.6.1.1, 2.6.2.1, 2.6.2.1, 2.6.3.1, 2.6.4.1 and 2.6.5.1.

In general, no field sampling is anticipated for this pilot study. All samples will be obtained either from sample archives for residential soils or from site representatives for on-smelter facility soils or materials or PAX. However, in the event that sampling is required for on-smelter facility soils or materials, sampling procedures are included in this project plan. All Standard Operating Procedures (SOPs) pertaining to sample collection are provided in Appendix A.

Each soil or material identified for investigation in this project plan was chosen based on two components: 1) arsenic concentration and 2) location of the sample, as reported in past sampling and analysis activities (USEPA 1998a, 1998b; USEPA 1999a). In general,

this biased approach to soil characterization will allow comparison of soil/materials that theoretically have the most distinct differences in physical and chemical makeup (high or intermediate versus low arsenic concentrations). This approach is believed to net optimal information regarding the physical and chemical attributes of each soil or material type and serve to measure the feasibility for these characteristics to be used as a diagnostic tool on a broader scale. Rationale and supporting study design Data Quality Objectives (DQOs) that are specific for each phase of the study are detailed in the subsequent sections.

2.1 Study Design Data Quality Objectives

USEPA has published a number of guidance documents on the DQO process (USEPA 1994, 1996, 1998d), and this project plan has been developed in accord with that guidance. In brief, the DQO process follows a seven-step procedure, as follows:

1) State the problem that the study is designed to address
2) Identify the decisions to be made with the data obtained
3) Identify the types of data inputs needed to make the decision
4) Define the bounds (in space and time) of the study
5) Define the decision rule which will be used to make decisions
6) Define the acceptable limits on decision errors
7) Optimize the design for obtaining data in an iterative fashion using information and DQOs identified in Steps 1-6

These steps are addressed for each activity planned as part of the pilot-scale soil characterization program. Note that the DQO process cites PARCC (precision, accuracy, representativeness, completeness and comparability) as a meaningful method for ensuring that all aspects of the study have been carefully reviewed and thought out. Study design elements of PARCC are provided in the subsequent sections in support of the DQO process. The elements of PARCC as they relate to specific quality assurance and quality control procedures are provided in Section 3.0 (Quality Assurance Project Plan [QAPP]). Each element of PARCC is defined below.

Precision: Precision is defined as the agreement between a set of replicate measurements without assumption or knowledge of the true value. It is a measure of agreement among individual measurements of the same characteristic under prescribed similar conditions.

Accuracy: Accuracy is a measure of the closeness of individual measurements to the "true" value. Accuracy usually is often expressed as a percentage of that known or true value.

Representativeness: Representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to heterogeneity of soils). It is important to determine whether samples evaluated for this investigation are representative at both levels.

Completeness: Completeness is defined as the ratio of valid measurements obtained during the study to the total number of measurements collected during the study. Completeness is achieved when a prescribed percentage of the valid measurements are obtained from the study.

Comparability: Comparability is defined as the measure of the confidence with which one data set or method can be compared to another.

2.1.1 Study Objective Hypotheses

An important part of the DQO process for study design is to establish the set of hypotheses that will identify a well-established end point from which data users are able to assess the success of the study. The set of null and alternative hypotheses for this study is provided in Table 2.1.1, along with conclusions that can be made based on whether the null hypothesis is rejected or has failed to be rejected.

The significance of observed differences between the parameters measured for residential soils and/or materials will be a qualitative determination, which uses professional judgement. Therefore, wherever use of professional judgment is cited in data evaluation, the procedures and/or decision-making criteria used to form conclusions about the data must be documented. Additionally, all conclusions made using professional judgment (as it pertains to characterization of physical soil attributes) will be peer-reviewed by a soil scientist.

Table 2.1.1: Study Objective Hypotheses [a]

Test	H_0 (Null Hypothesis)	H_1(Alternative Hypothesis)	Conclusion if H_0 not rejected	Conclusion if H_0 Rejected
Hypothesis 1	Physical characteristics (listed in Section 2.3) of soils having high (>900 ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having low (<70ppm) levels of arsenic.	Physical characteristics (listed in Section 2.3) of soils having high levels of arsenic ***are*** significantly different than characteristics of soils having low levels of arsenic.	*The physical characteristics measured in soils **cannot** be differentiated between soils with high and low arsenic levels.*	*The physical characteristics measured in soils **can** be differentiated between soils with high and low arsenic levels.*
Hypothesis 2	Physical characteristics (listed in Section 2.3) of soils having high (>900 ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having intermediate (>150-≤450ppm) levels of arsenic.	Physical characteristics (listed in Section 2.3) of soils having high levels of arsenic ***are*** significantly different than characteristics of soils having intermediate levels of arsenic.	*The physical characteristics measured in soils **cannot** be differentiated between soils with high and intermediate arsenic levels.*	*The physical characteristics measured in soils **can** be differentiated between soils with high and intermediate arsenic levels.*
Hypothesis 3	Physical characteristics (listed in Section 2.3) of soils having Intermediate (>150-≤450ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having low levels of arsenic.	Physical characteristics (listed in Section 2.3) of soils having intermediate levels of arsenic ***are*** significantly different than characteristics of soils having low levels of arsenic.	*The physical characteristics measured in soils **cannot** be differentiated between soils with intermediate and low arsenic levels.*	*The physical characteristics measured in soils **can** be differentiated between soils with intermediate and low arsenic levels.*
Hypothesis 4	Chemical characteristics of soils having high (>900 ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having low (<70ppm) levels of arsenic.	Chemical characteristics of soils having high levels of arsenic ***are*** significantly different than characteristics of soils having low levels of arsenic.	*The chemical characteristics measured in soils **cannot** be differentiated between soils of high and low arsenic levels.*	*The chemical characteristics measured in soils **can** be differentiated between soils of high and low arsenic levels.*
Hypothesis 5	Chemical characteristics of soils having high (>900 ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having intermediate (>150-≤450ppm) levels of arsenic.	Chemical characteristics of soils having high levels of arsenic ***are*** significantly different than characteristics of soils having intermediate levels of arsenic.	*The chemical characteristics measured in soils **cannot** be differentiated between soils of high and intermediate arsenic levels.*	*The chemical characteristics measured in soils **can** be differentiated between soils of high and intermediate arsenic levels.*

Table 2.1.1: Study Objective Hypotheses [a]

Test	H_0 (Null Hypothesis)	H_1(Alternative Hypothesis)	Conclusion if H_0 not rejected	Conclusion if H_0 Rejected
Hypothesis 6	Chemical characteristics of soils having intermediate (>150-≤450ppm) levels of arsenic ***are not*** significantly different than characteristics of soils having low (<70ppm) levels of arsenic.	Chemical characteristics of soils having intermediate levels of arsenic ***are*** significantly different than characteristics of soils having low levels of arsenic.	*The chemical characteristics measured in soils **cannot** be differentiated between soils of intermediate and low arsenic levels.*	*The chemical characteristics measured in soils **can** be differentiated between soils of intermediate and low arsenic levels.*
Hypothesis 7	The "fingerprint" developed for physical characteristics of soils having high levels of arsenic **is not** significantly different than the "fingerprint" developed for the physical characteristics of potential source materials.	The "fingerprint" developed for physical characteristics of soils having high levels of arsenic **is** significantly different than the "fingerprints" developed for the physical characteristics of potential source materials.	*Data collected from the physical characteristics measured in soils are not sufficient for use in source attribution.*	*Data collected from the physical characteristics measured in soils are sufficient for use in source attribution.*
Hypothesis 8	The "fingerprint" developed for physical characteristics of soils having intermediate levels of arsenic **is not** significantly different than the "fingerprint" developed for the physical characteristics of potential source materials.	The "fingerprint" developed for physical characteristics of soils having intermediate levels of arsenic **is** significantly different than the "fingerprints" developed for the physical characteristics of potential source materials.	*Data collected from the physical characteristics measured in soils **are not** sufficient for use in source attribution.*	*Data collected from the physical characteristics measured in soils **are** sufficient for use in source attribution.*
Hypothesis 9	The "fingerprint" developed for physical characteristics of soils having low levels of arsenic **is not** significantly different than the "fingerprint" developed for the physical characteristics of potential source materials.	The "fingerprint" developed for physical characteristics of soils having low levels of arsenic **is** significantly different than the "fingerprints" developed for the physical characteristics of potential source materials.	*Data collected from the physical characteristics measured in soils **are not** sufficient for use in source attribution.*	*Data collected from the physical characteristics measured in soils **are** sufficient for use in source attribution.*

Table 2.1.1: Study Objective Hypotheses [a]

Test	H_0 (Null Hypothesis)	H_1(Alternative Hypothesis)	Conclusion if H_0 not rejected	Conclusion if H_0 Rejected
Hypothesis 10	The "fingerprint" developed for chemical characteristics of soils having high levels of arsenic **is not** significantly different than the "fingerprints" developed for the chemical characteristics of potential source materials.	The "fingerprint" developed for chemical characteristics of soils having high levels of arsenic **is** significantly different than the "fingerprint" developed for the chemical characteristics of potential source materials.	*Data collected from the chemical charcteristics measured in soils **are not** sufficient for use in source attribution.*	*Data collected from the chemical charcteristics measured in soils **are** sufficient for use in source attribution.*
Hypothesis 11	The "fingerprint" developed for chemical characteristics of soils having intermediate levels of arsenic **is not** significantly different than the "fingerprints" developed for the chemical characteristics of potential source materials.	The "fingerprint" developed for chemical characteristics of soils having intermediate levels of arsenic **is** significantly different than the "fingerprint" developed for the chemical characteristics of potential source materials.	*Data collected from the chemical charcteristics measured in soils **are not** sufficient for use in source attribution.*	*Data collected from the chemical charcteristics measured in soils **are** sufficient for use in source attribution.*
Hypothesis 12	The "fingerprint" developed for chemical characteristics of soils having low levels of arsenic **is not** significantly different than the "fingerprints" developed for the chemical characteristics of potential source materials.	The "fingerprint" developed for chemical characteristics of soils having low levels of arsenic **is** significantly different than the "fingerprint" developed for the chemical characteristics of potential source materials.	*Data collected from the chemical charcteristics measured in soils **are not** sufficient for use in source attribution.*	*Data collected from the chemical charcteristics measured in soils **are** sufficient for use in source attribution.*

[a] - the significance of observed differences will be a qualitative determination, using a weight-of-evidence approach.

All conclusions will be peer-reviewed by a soil scientist.

2.2 Sample Selection

As mentioned previously, field sampling is generally not required for residential soils tested as part of this pilot study. All residential soils identified for evaluation will be obtained from soil archives. These soils were collected in previous soil studies (USEPA 1999a) which have been maintained under chain-of-custody by USEPA, Region 8. On-smelter facility soils or materials and PAX will be obtained from appropriate resources. ASARCO will provide stack and soil samples from the Globe smelter. The USEPA Region 8 will seek the cooperation of other parties in obtaining soil and material samples collected from the Globe, Omaha-Grant, Argo and Tacoma smelters. All archived candidate samples, and any new samples collected for this study, must have chain-of-custody documentation from sample collection to disposal.

Table 2.2.1 summarizes the estimated number of sample locations planned for the pilot-scale investigation. Each residential location coincides with 1 composite sample that consists of 12-15 sub-samples. Details regarding assignment of each type of sample presented in the table are provided in the subsections that follow. The method that will be used for comparison of the results for these samples is provided in each sub-section that outlines Data Use.

Table 2.2.1 – Estimated Quantities and Distribution of Solid Materials

Category[a]	Sample Locations (N)		
	Residential Site	On-Smelter Facility[b]	PAX
Low Arsenic Soil (≤70 ppm)	4[c]	--	--
Intermediate Soil (>150-≤450 ppm)	3	--	--
High Arsenic Soil (>900 ppm)	3	5	--
Randomly Selected Soil	20	--	--
PAX	--	--	1

-- Not Applicable

a – All soil samples collected from the 0-2 inch horizon will be bulk soil (sieved to <2 mm), or fines soil (sieved to < 250 µm) (bioaccessibility).

b – This assumes a single smelter site (Globe Plant) will provide samples. Three sample locations will be soil samples. Two sample locations will be from other high arsenic materials such as stack material, arsenic trioxide product, or flue dust. This number may be adjusted if samples from other sites are made available.

c – One composite sample collected at the VBI70 Phase 3 soil baseline site will be included in the "low" category. Arsenic concentration in this soil is about 8 ppm, which is the average from two different analytical methods.

The sub-samples (N=12-15) of surface soil selected for evaluation have been chosen using 3 criteria: 1) samples have been collected at regions within a residence that are within each range of arsenic concentration listed in Table 2.2.1 (high, intermediate, or low); 2) samples of similar concentration are typically adjacent to each other (i.e., they are all in about the same region of the property); 3) arsenic levels in selected samples are

usually within 3 times of each other. All sub-samples will be composited and the composite sample will be submitted for physical and chemical analysis.

In the event that the necessary potential source soil and/or materials are not already maintained in the sample archives under chain-of-custody, sampling will be required. Note that samples should be field sieved (<2 mm) but should not be sieved further to <250 μm unless prescribed in the specified methodology (e.g., *in vitro* bioaccessibility). Procedures for collection of surface soil samples are outlined in the Surface Soil Sampling for Metals SOP (Appendix A). Procedures for collection of samples from the arsenic kitchen(s) are provided in the Test Pit Sampling at Smelter Facilities SOP (Appendix A).

2.2.1 Residential Soils – Physical and Chemical Soil Characterization

As seen in Table 2.2.1, four different types of residential soils are planned for investigation: High Arsenic properties, Intermediate Arsenic properties, Low Arsenic properties, and Randomly Selected properties. Rationale for inclusion of each soil type is as follows.

1) High Arsenic properties have been intensively studied and are known to have elevated levels of arsenic (> 900 ppm). Characterization of the soils containing high arsenic levels is key for comparison to potential sources of arsenic.

2) Intermediate arsenic properties have been intensively studied, and investigation of soils having intermediate levels of arsenic (>150-≤450 ppm) will provide information on areas that are clearly above the low arsenic properties, but may be different in physical and chemical characteristics than the high arsenic and low arsenic properties. Characterization of the soils containing intermediate arsenic levels is key for comparison to potential sources of arsenic.

3) Low Arsenic properties have been intensively studied and are known to have arsenic levels below 70 ppm. Characterization of soils having low arsenic levels is important for comparison to High and Intermediate arsenic properties and to potential sources having high arsenic levels.

4) Randomly Selected properties have not been intensively studied but an estimate of the arsenic levels at these properties has been obtained during Phases I and II Field Sampling Activities (USEPA 1998a, 1998b). These properties have been selected to determine if the soil characteristics vary across the VBI70 site.

Approximately 30 residential sample locations have been identified for investigation, three each from High and Intermediate properties, four from Low Arsenic properties, and the remaining (20) from Randomly Selected Properties. For each residential location

identified as a High, Intermediate, or Low Arsenic property, two individual samples will be selected. One sample from the residence of interest (termed "focal" property) and one sample from a residence adjacent to the focal property (termed "adjacent" property) will be obtained. Each sample will be a composite of about 12-15 sub-samples. Samples for the Randomly Selected Properties will consist of a single soil sample location, because these residences were not sampled intensively. Data used for identification of residential soils were obtained from previous studies: High, Intermediate, and Low Arsenic properties (USEPA 1999) and Randomly Selected properties (USEPA 1998a, 1998b).

High Arsenic Properties

Sample locations for High arsenic properties will be identified at regions where: 1) multiple contiguous samples were found to have arsenic concentrations above 900 ppm; and 2) "boundary effects" are observed between the focal and adjacent properties. For the purposes of this project plan, boundary effects will be defined as areas where sharp changes in concentration across several samples are observed. About 12-15 sub-samples from the focal property and 12-15 from the adjacent region will be identified in areas where boundary effects are observed, and will then be composited to yield two individual samples (focal and adjacent) for each property location.

Intermediate Properties

Samples at Intermediate arsenic properties will be identified at regions where: 1) multiple contiguous samples were found to have arsenic concentrations of >150-≤450 ppm; and 2) "boundary effects" are observed between the focal and adjacent properties. For the purposes of this project plan, boundary effects will be defined as areas where sharp changes in concentration across several samples are observed. About 12-15 sub-samples will be identified on properties where boundary effects are observed, and will then be composited to yield two individual samples (focal and adjacent) for each property location.

Low Arsenic Properties

Samples at Low Arsenic properties will be identified at focal properties where arsenic levels were measured to below 70 ppm. This level was chosen based on the results of previous studies, (USEPA 1998a, 1998b, 1999a) which typically reported a detection limit of about 46 ppm for arsenic. Focal properties selected for this category which are shown in Maps 2, 6 and 7 (Figures 2.2.2, 2.2.5 and 2.2.6) were stratified so that two of the three properties (Figures 2.2.5 and 2.2.6) have samples with arsenic concentrations that are near the reporting limit. The third property (Figure 2.2.2) reports arsenic levels closer to, but less than 70 ppm. Unlike the High and Intermediate arsenic properties, the adjacent property for the Low arsenic properties will also have low arsenic levels.

One composite sample collected as part of the Phase III Field Investigation (USEPA 1999b) will be included in this category. This sample was analyzed by neutron activation, and was found to have an arsenic concentration of 7.9 ppm. This sample will also be characterized using the physical and chemical parameters outlined in Section 2.5 and 2.6 to provide information on the characteristics of site soils with very low arsenic levels.

Randomly Selected Properties

Sample locations for Randomly Selected properties will be identified using data obtained from the Phase I and Phase II Field Sampling Activity (USEPA1998a, 1998b). A list of 20 sample locations were randomly selected from these residences.

Residential soil samples from each of the categories listed in Table 2.2.1 have been selected, and their location and previously measured arsenic concentration are listed in Table 2.2.2. In order to maintain confidentiality, the addresses for residences from which soils samples will be analyzed have been assigned a Residential Location Code. Each sample location has been identified as either a focal and adjacent property. Refer to Figure 2.2.8 for a spatial representation of properties included in the Randomly Selected category.

Table 2.2.2: Proposed Residential Soil Sample Locations

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm) for Focal Property	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc.(ppm) for Adjacent Property
High (>900 ppm)	C	Sub-sample 1	1	19,04	2526	17,01	23
		Sub-sample 2		19,05	1272	17,02	23
		Sub-sample 3		19,06	1348	18,01	63
		Sub-sample 4		19,07	1610	18,02	53
		Sub-sample 5		20,03	1039	19,01	59
		Sub-sample 6		21,05	1293	19,02	23
		Sub-sample 7		21,06	1222	20,02	57
		Sub-sample 8		21,07	1257	21,00	69
		Sub-sample 9		22,04	1741	21,01	23
		Sub-sample 10		22,05	1156	21,02	23
		Sub-sample 11		23,03	1014	23,00	23
		Sub-sample 12		23,04	1464	23,01	23
		Sub-sample 13		23,05	1049	24,00	23
		Sub-sample 14		23,06	1115	24,01	23
		Sub-sample 15		24,04	902	24,02	53
High (>900 ppm)	A	Sub-sample 1	2	1,10	3449	0,13	23
		Sub-sample 2		1,11	1716	0,15	66
		Sub-sample 3		1,12	6374	1,14	23
		Sub-sample 4		2,10	2719	2,13	64
		Sub-sample 5		2,11	3208	2,14	23
		Sub-sample 6		2,12	4219	2,15	46
		Sub-sample 7		3,10	1917	3,13	50
		Sub-sample 8		3,11	1676	3,14	23
		Sub-sample 9		3,12	1409	3,15	23
		Sub-sample 10		4,10	2486	4,13	70
		Sub-sample 11		4,11	2032	4,14	23
		Sub-sample 12		4,12	2665	4,15	23
		Sub-sample 13		5,10	5382	5,13	23
		Sub-sample 14		5,12	1962	5,14	23
		Sub-sample 15		6,11	6887	5,15	51

Table 2.2.2: Proposed Residential Soil Sample Locations

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm) for Focal Property	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc.(ppm) for Adjacent Property
High (>900 ppm)	B	Sub-sample 1	5	10,03	3041	12,00	56
		Sub-sample 2		11,03	5429	12,01	23
		Sub-sample 3		11,05	2456	12,02	54
		Sub-sample 4		11,06	2476	13,02	65
		Sub-sample 5		12,03	2272	14,00	23
		Sub-sample 6		12,06	1651	14,01	23
		Sub-sample 7		12,07	1701	15,01	23
		Sub-sample 8		13,05	2122	16,00	23
		Sub-sample 9		13,07	1917	16,01	23
		Sub-sample 10		14,05	3041	16,02	23
		Sub-sample 11		14,07	2122	27,01	64
		Sub-sample 12		14,08	3095	28,00	68
		Sub-sample 13		15,03	2461	28,01	68
		Sub-sample 14		15,06	2097	31,00	62
		Sub-sample 15		16,04	3796	31,01	55
Intermediate (>150 -≤450ppm)	D	Sub-sample 1	3	19,08	419	***	***
		Sub-sample 2		20,09	435	19,10	23
		Sub-sample 3		21,08	390	21,10	23
		Sub-sample 4		21,09	257	22,10	23
		Sub-sample 5		22,08	253	23,10	23
		Sub-sample 6		22,09	405	24,10	59
		Sub-sample 7		25,02	183	25,00	55
		Sub-sample 8		25,03	309	26,00	49
		Sub-sample 9		25,04	432	26,09	53
		Sub-sample 10		25,05	330	26,10	23
		Sub-sample 11		25,06	324	27,00	55
		Sub-sample 12		25,08	363	27,02	23
		Sub-sample 13		26,02	176	27,03	57
		Sub-sample 14		26,05	375	27,05	23
		Sub-sample 15		26,08	202	27,06	56

Table 2.2.2: Proposed Residential Soil Sample Locations

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm) for Focal Property	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc.(ppm) for Adjacent Property
Intermediate (>150 -≤450ppm)	B	Sub-sample 1	5	0,07	351	17,01	23
		Sub-sample 2		0,09	303	17,02	23
		Sub-sample 3		0,10	390	18,01	63
		Sub-sample 4		0,11	213	18,02	53
		Sub-sample 5		0,12	233	19,01	59
		Sub-sample 6		1,03	255	19,02	23
		Sub-sample 7		1,06	324	20,02	57
		Sub-sample 8		1,07	321	21,00	69
		Sub-sample 9		1,10	293	21,01	23
		Sub-sample 10		1,12	205	21,02	23
		Sub-sample 11		2,07	410	23,00	23
		Sub-sample 12		2,09	341	23,01	23
		Sub-sample 13		2,10	346	24,00	23
		Sub-sample 14		2,11	181	24,01	23
		Sub-sample 15		2,12	215	24,02	53
Intermediate (>150 -≤450ppm)	H	Sub-sample 1	8	13,06	240	15,04	23
		Sub-sample 2		13,07	343	15,09	67
		Sub-sample 3		13,08	235	15,18	23
		Sub-sample 4		13,10	201	15,19	23
		Sub-sample 5		13,20	161	15,22	23
		Sub-sample 6		13,21	169	16,03	23
		Sub-sample 7		13,22	394	16,04	23
		Sub-sample 8		13,23	337	16,07	23
		Sub-sample 9		13,24	310	16,09	62
		Sub-sample 10		13,25	176	16,15	67
		Sub-sample 11		14,04	243	16,17	23
		Sub-sample 12		14,06	299	16,18	69
		Sub-sample 13		14,07	378	16,19	23
		Sub-sample 14		14,08	268	16,20	68
		Sub-sample 15		14,20	159	16,21	68

Table 2.2.2: Proposed Residential Soil Sample Locations

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm) for Focal Property	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc.(ppm) for Adjacent Property
Low (<70 ppm)	A	Sub-sample 1	2	***	***	***	***
		Sub-sample 2		***	***	***	***
		Sub-sample 3		***	***	35,05	23
		Sub-sample 4		13,10	54	35,06	23
		Sub-sample 5		14,09	49	35,07	23
		Sub-sample 6		14,10	51	35,08	23
		Sub-sample 7		14,11	23	35,09	23
		Sub-sample 8		15,11	23	35,10	23
		Sub-sample 9		15,12	23	35,12	23
		Sub-sample 10		16,11	23	36,02	23
		Sub-sample 11		17,11	56	36,10	23
		Sub-sample 12		17,12	23	36,12	23
		Sub-sample 13		18,10	23	37,02	23
		Sub-sample 14		20,13	23	37,11	23
		Sub-sample 15		21,12	23	37,12	23
Low (<70 ppm)	G	Sub-sample 1	6	10,16	58	***	***
		Sub-sample 2		10,18	57	***	***
		Sub-sample 3		10,21	48	***	***
		Sub-sample 4		10,22	55	14,09	23
		Sub-sample 5		10,23	61	14,10	23
		Sub-sample 6		10,24	51	14,11	23
		Sub-sample 7		11,17	60	14,12	67
		Sub-sample 8		11,18	67	14,13	23
		Sub-sample 9		11,25	46	14,14	23
		Sub-sample 10		12,15	23	14,15	23
		Sub-sample 11		12,16	46	14,16	23
		Sub-sample 12		12,17	23	14,17	23
		Sub-sample 13		12,19	47	14,19	56
		Sub-sample 14		12,20	23	14,21	23
		Sub-sample 15		12,22	54	14,24	23

Table 2.2.2: Proposed Residential Soil Sample Locations

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm) for Focal Property	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc.(ppm) for Adjacent Property
Low (<70 ppm)	F	Sub-sample 1	7	***	***	2,01	55
		Sub-sample 2		8,16	23	2,02	65
		Sub-sample 3		8,17	62	4,01	23
		Sub-sample 4		8,20	62	4,02	46
		Sub-sample 5		8,22	23	4,06	54
		Sub-sample 6		9,07	23	4,21	23
		Sub-sample 7		9,08	58	4,22	49
		Sub-sample 8		9,09	51	4,23	23
		Sub-sample 9		9,12	23	5,21	23
		Sub-sample 10		9,14	23	5,22	49
		Sub-sample 11		9,15	23	5,23	23
		Sub-sample 12		9,16	23	6,06	23
		Sub-sample 13		9,17	23	6,21	46
		Sub-sample 14		9,18	51	6,22	23
		Sub-sample 15		9,19	68	6,23	23

Table 2.2.2 (cont'd)

Category	Residential Location Code	Sample Description	Map No.[a]	Map (X,Y) Coordinates for Focal Property	Arsenic Conc. (ppm)	Map (X,Y) Coordinates for Adjacent Property	Arsenic Conc. (ppm)
Randomly Selected Soils[b]	G	Grab Sample	--	--	<44	--	--
	H	Grab Sample	--	--	<44	--	--
	I	Grab Sample	--	--	<44	--	--
	J	Grab Sample	--	--	58	--	--
	K	Grab Sample	--	--	<44	--	--
	L	Grab Sample	--	--	<57	--	--
	M	Grab Sample	--	--	<44	--	--
	N	Grab Sample	--	--	<44	--	--
	O	Grab Sample	--	--	<44	--	--
	P	Grab Sample	--	--	<44	--	--
	Q	Grab Sample	--	--	<57	--	--
	R	Grab Sample	--	--	<44	--	--
	S	Grab Sample	--	--	<44	--	--
	T	Grab Sample	--	--	<44	--	--
	U	Grab Sample	--	--	<57	--	--
	V	Grab Sample	--	--	<44	--	--
	W	Grab Sample	--	--	<57	--	--
	X	Grab Sample	--	--	<57	--	--
	Y	Grab Sample	--	--	<57	--	--
	Z	Grab Sample	--	--	<57	--	--

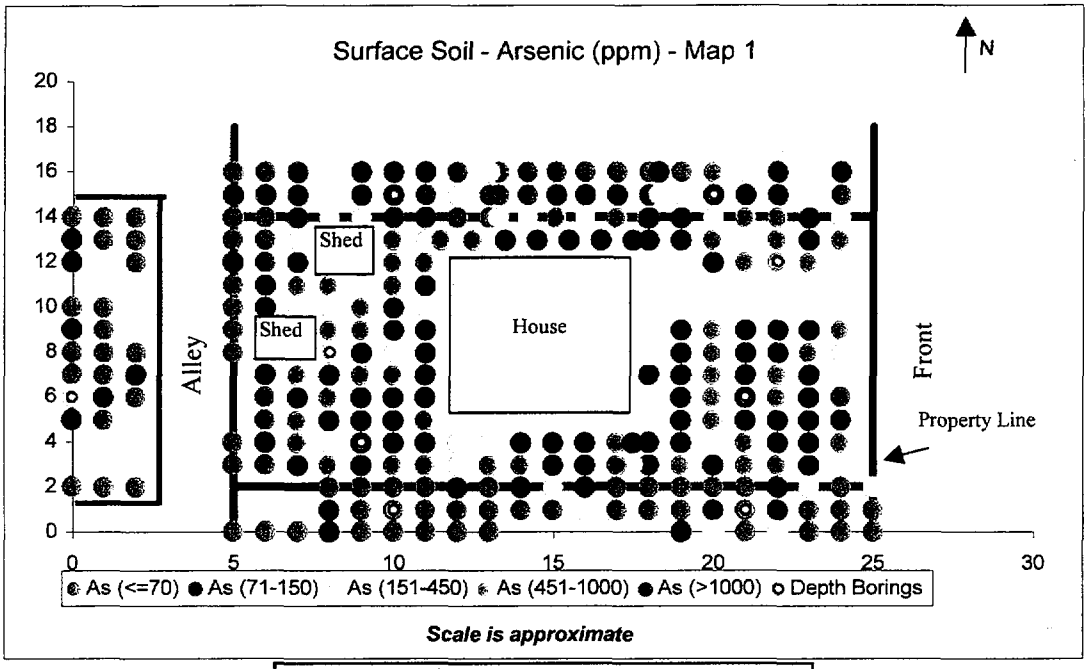
-- Not Applicable

[a] See Figures 2.2.1 to 2.2.7 for more information.

[b] See Figure 2.2.8 for more information.

*** No other sample available that meets selection criteria.

Figure 2.2.1. Surface Soil and Depth Profile for Arsenic Location 1



Summary Statistics	
N= 125 samples	Min= 9 ppm
Mean= 895 ppm	Max= 3105 ppm

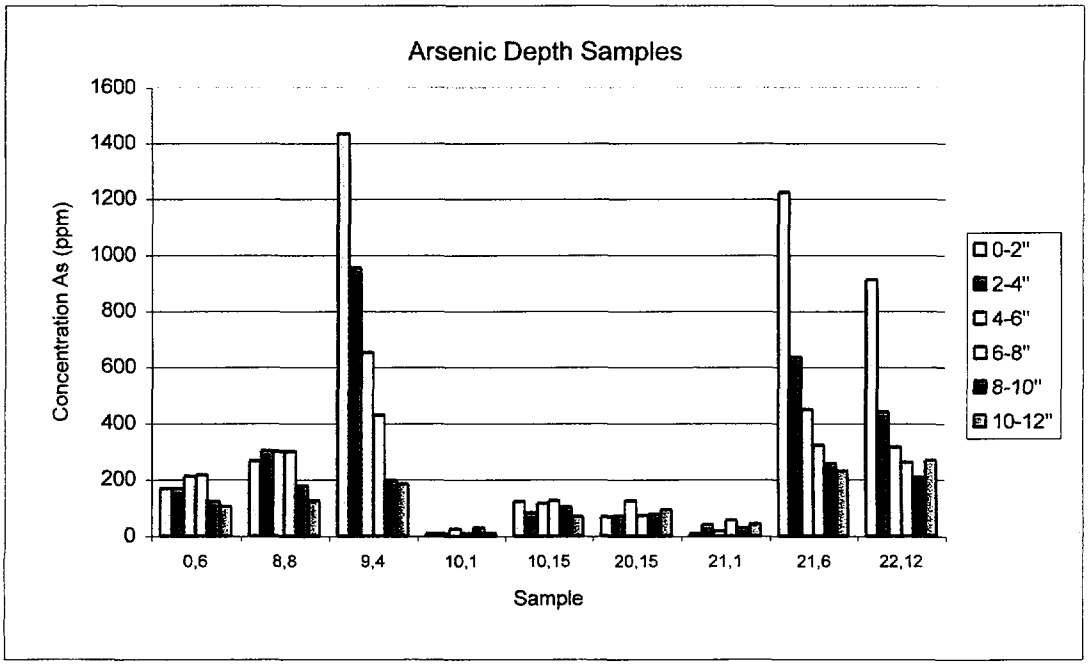
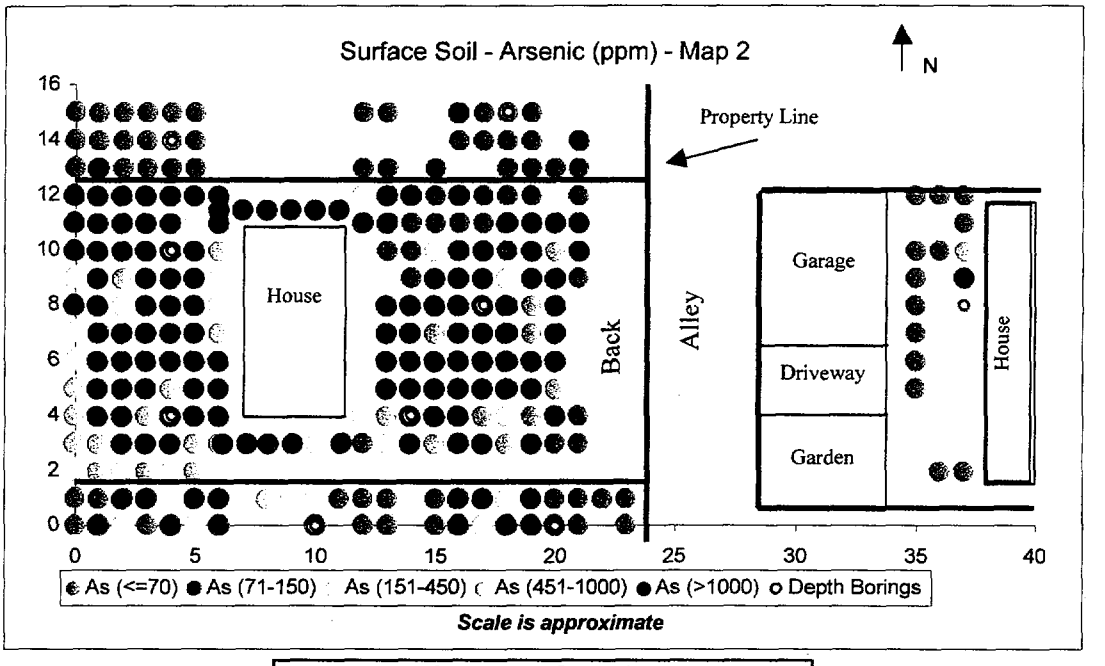


Figure 2.2.2 Surface Soil and Depth Profile for Arsenic
Location 2



Summary Statistics	
N= 163 samples	Min= 9 ppm
Mean= 1803 ppm	Max= 11785 ppm

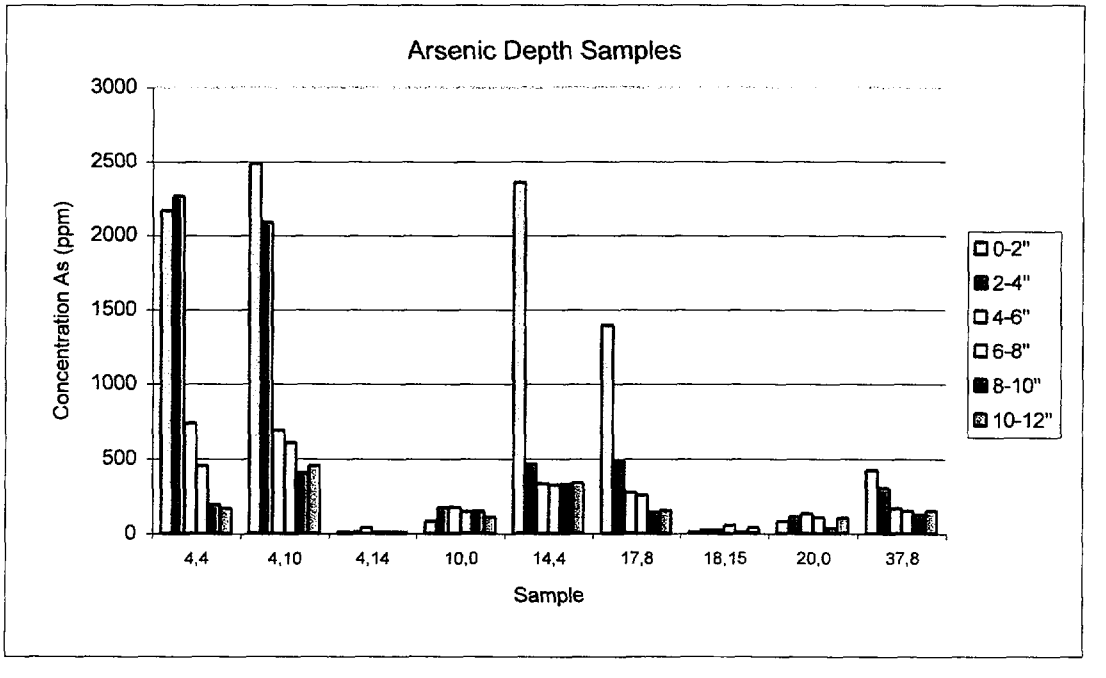
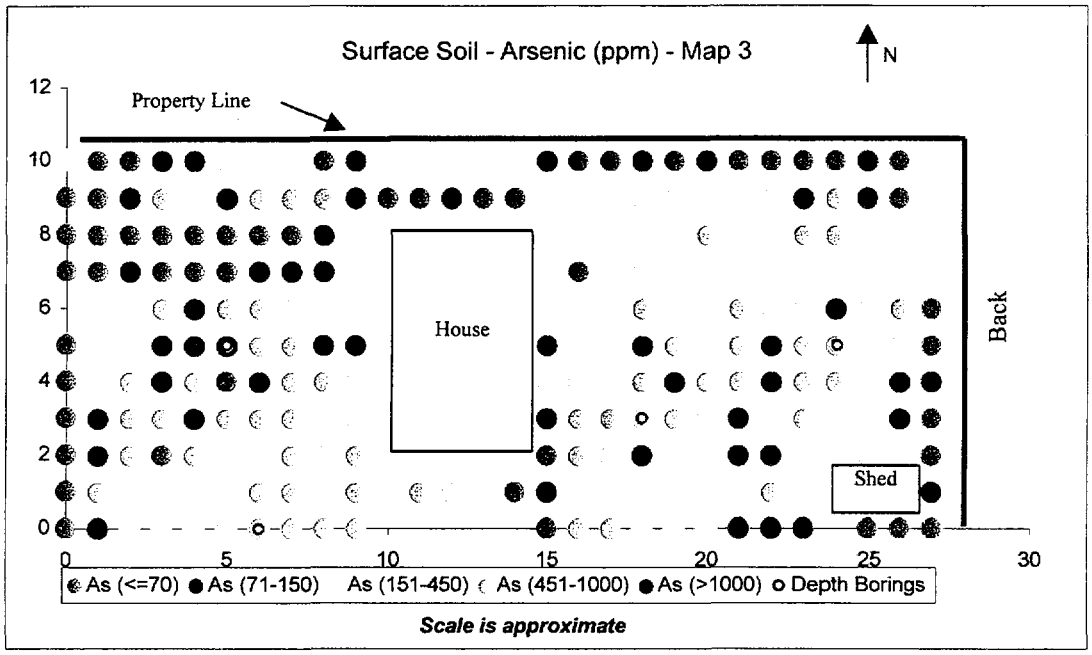


Figure 2.2.3. Surface Soil and Depth Profile for Arsenic
Location 3



Summary Statistics	
N= 218 samples	Min= 9 ppm
Mean= 389 ppm	Max= 2729 ppm

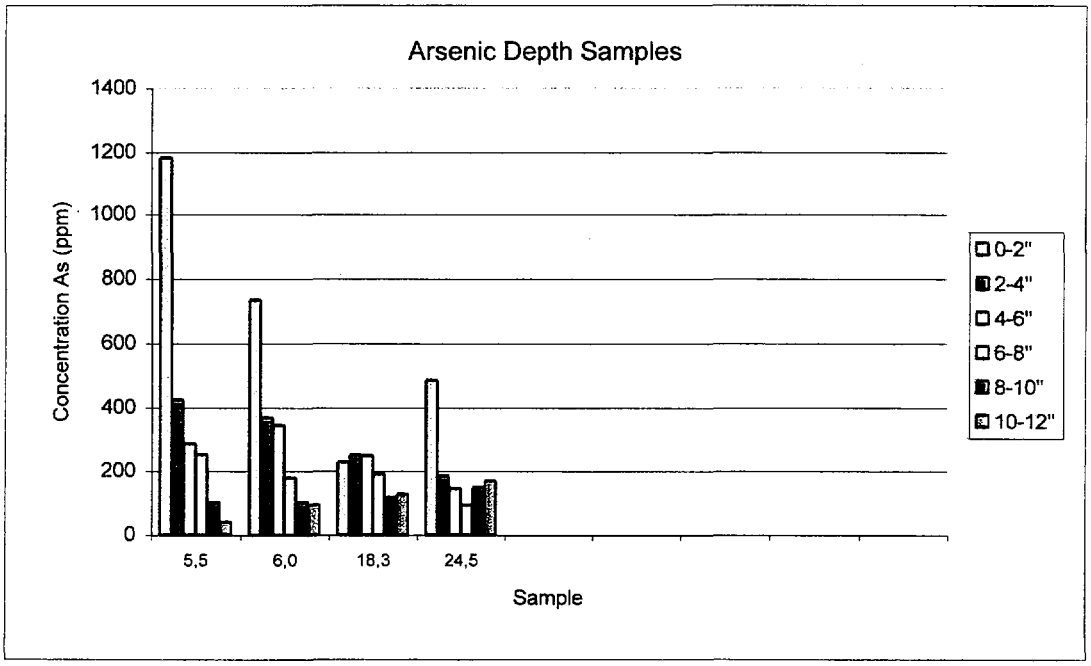
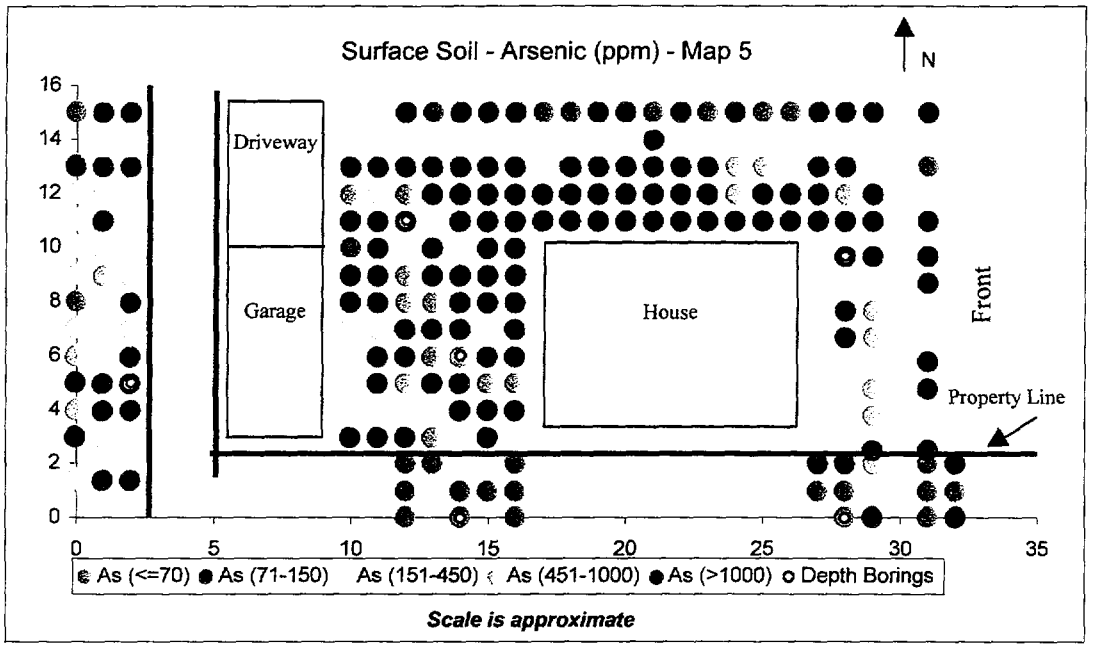


Figure 2.2.4 Surface Soil and Depth Profile for Arsenic
Location 5



Summary Statistics	
N= 92 samples	Min= 29 ppm
Mean= 1971 ppm	Max= 13171 ppm

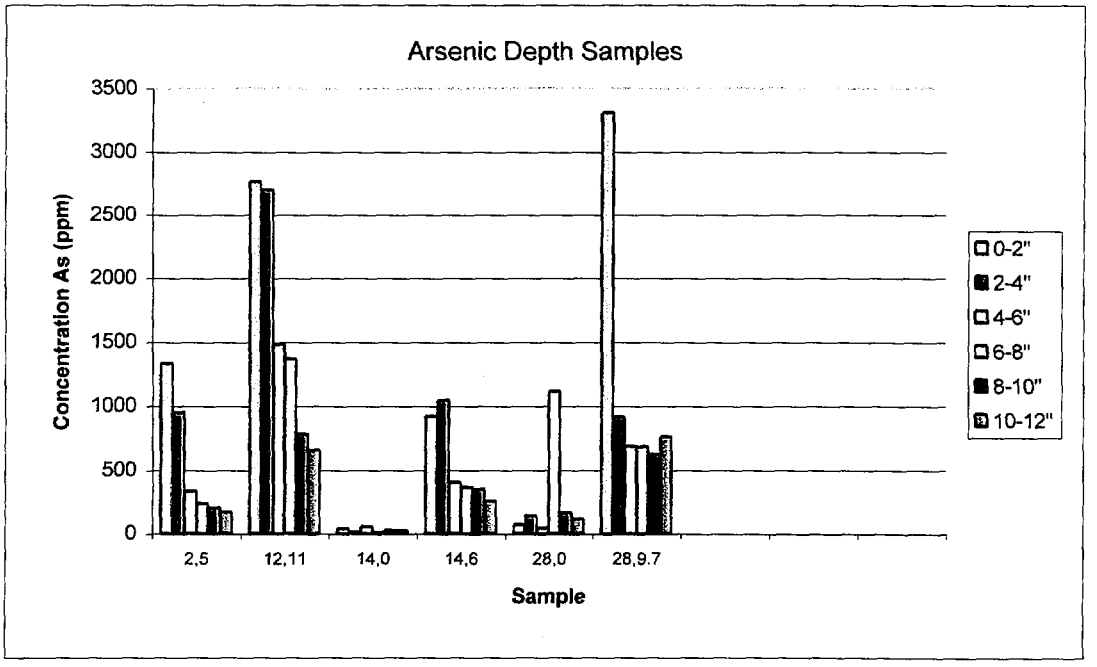
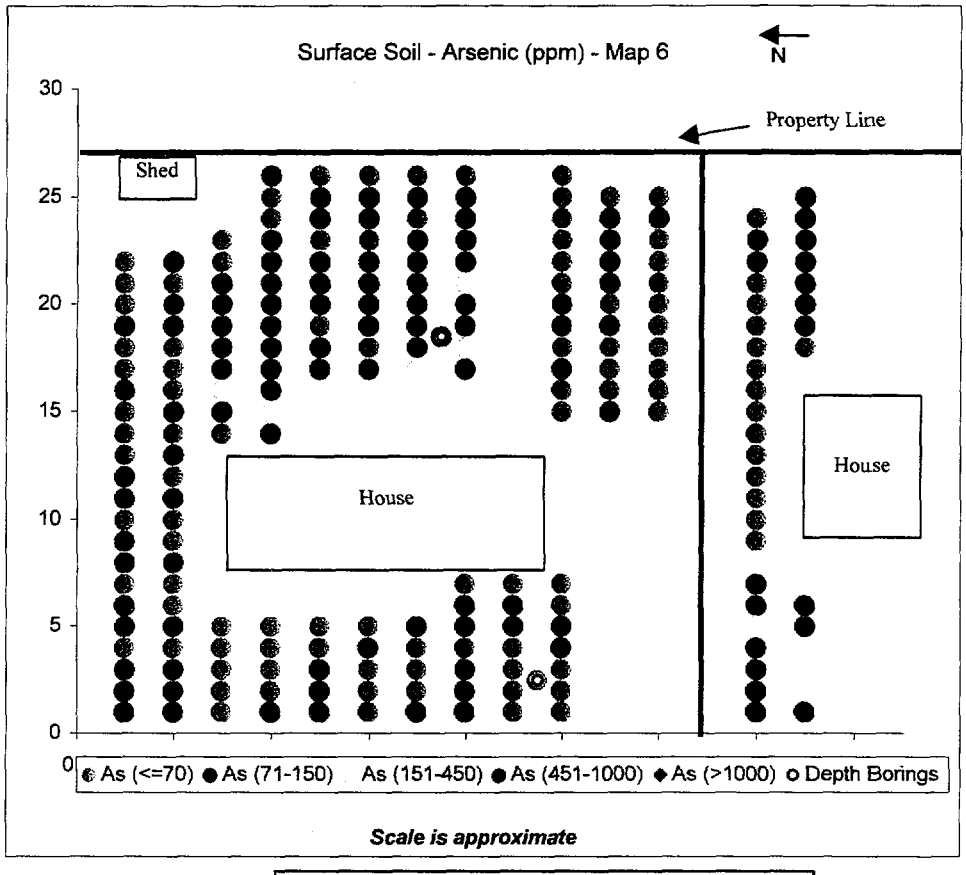


Figure 2.2.5 Surface Soil and Depth Profile for Arsenic
Location 6



Summary Statistics	
N= 190 samples	Min= 9 ppm
Mean= 78 ppm	Max= 343 ppm

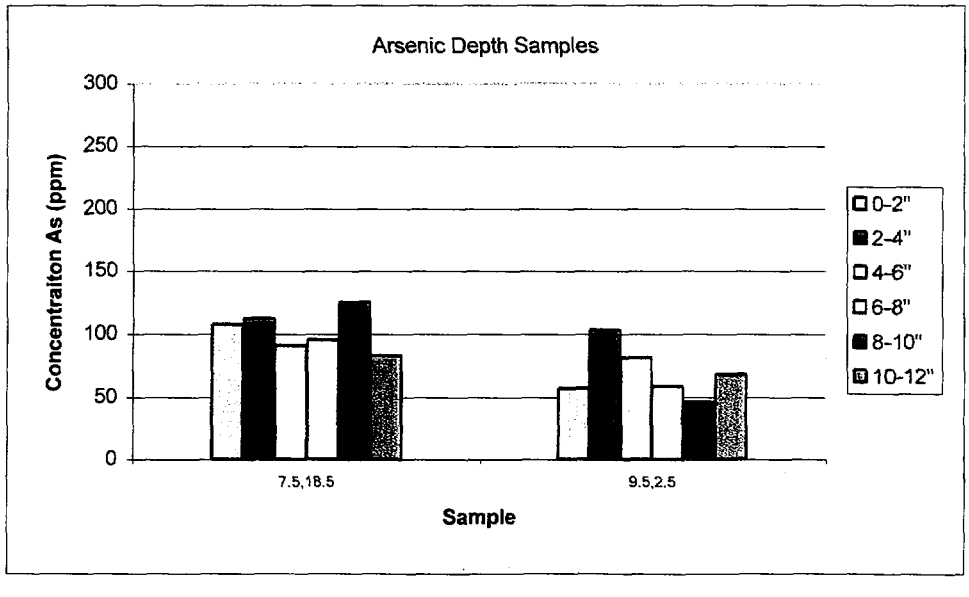
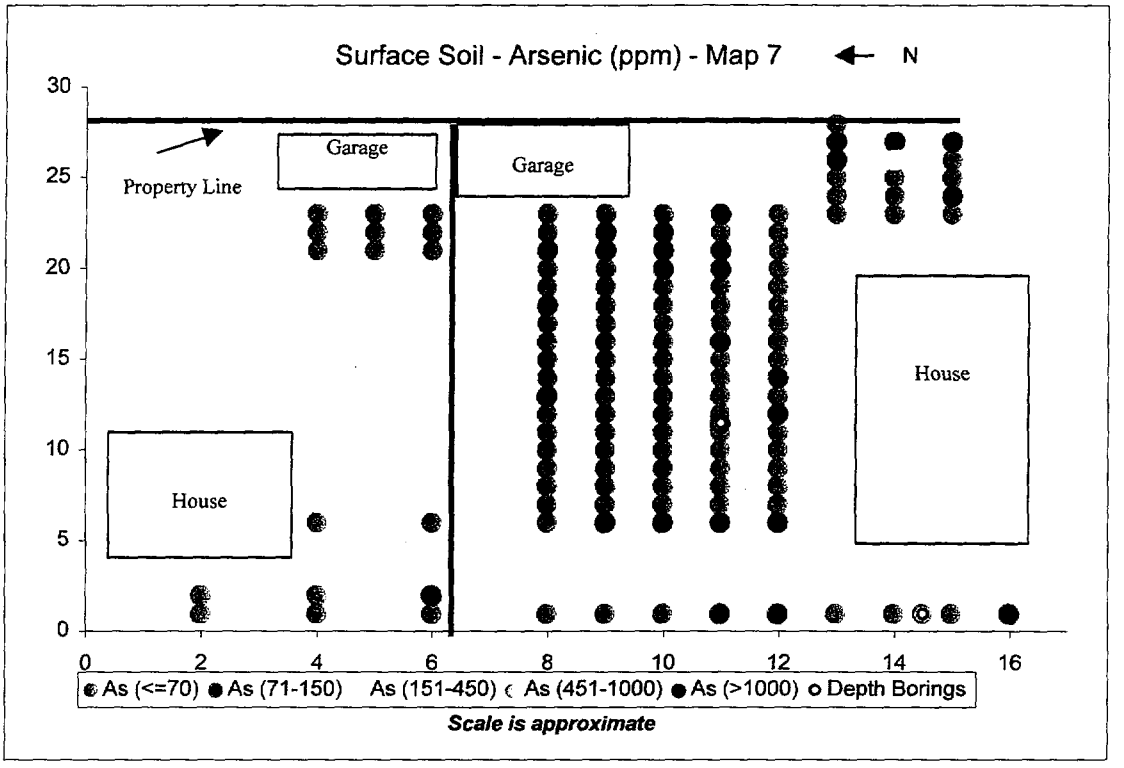


Figure 2.2.6 Surface Soil and Depth Profile for Arsenic
Location 7



Summary Statistics	
N= 116 samples	Min= 9 ppm
Mean= 48 ppm	Max= 164 ppm

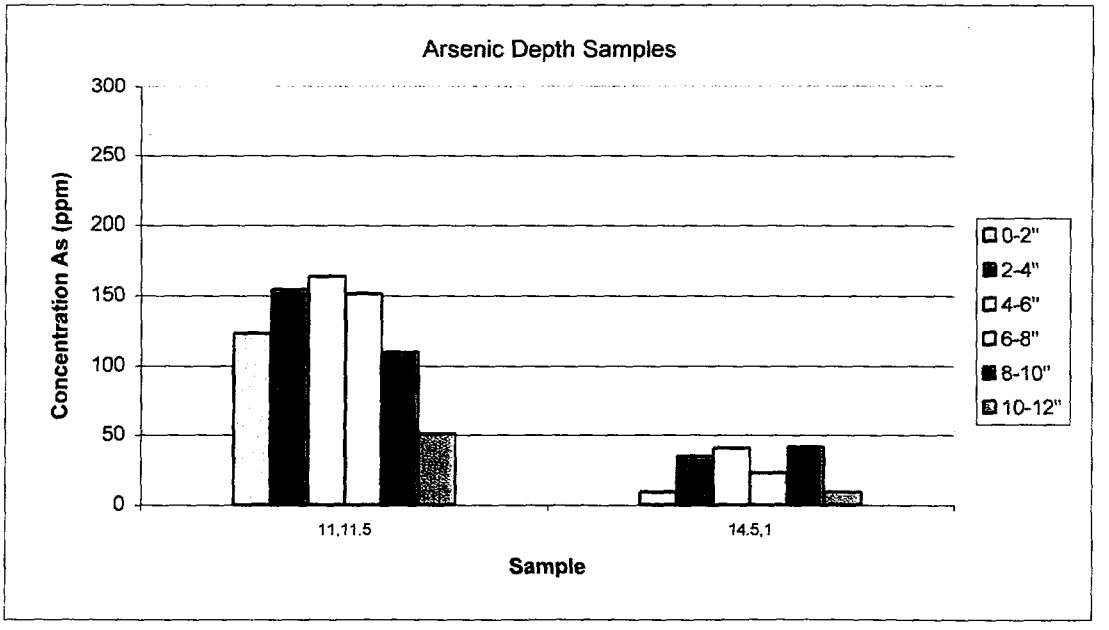
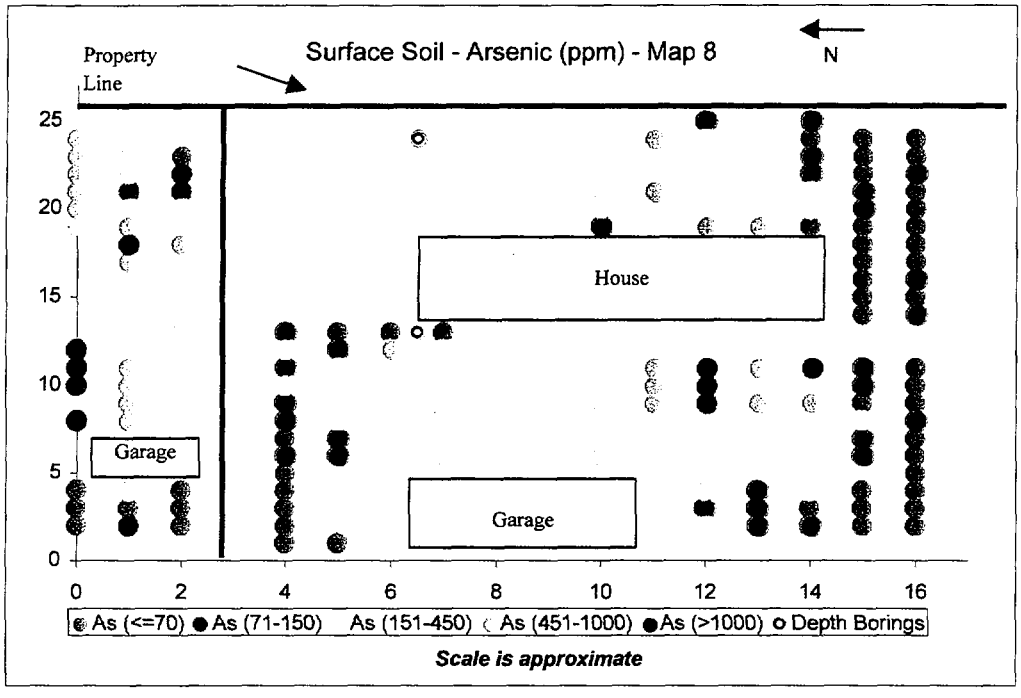
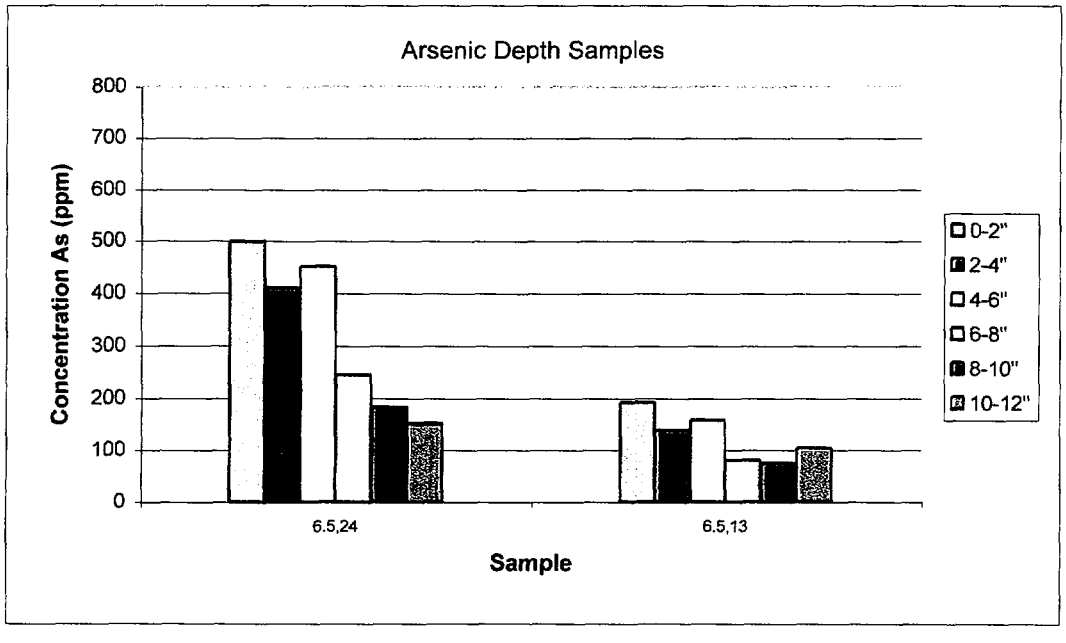


Figure2.2.7 Surface Soil and Depth Profile for Arsenic Location 8



Summary Statistics	
N= 158 samples	Min= 9 ppm
Mean= 246 ppm	Max= 1716 ppm



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2.2.2 Potential Source Materials

Any source material that may be attributable to arsenic contamination of residential soils at the VBI70 site is expected have high (>1000 ppm) arsenic levels. Potential source materials identified in the Conceptual Site Model (CSM) (Figure 2.2.9) are from smelter-related activities. In addition, USEPA is investigating the possibility that arsenical herbicide (e.g., PAX) may also be responsible for the random occurrence of arsenic hot spots about the VBI70 site. For this study, a representative sample of PAX will be used to characterize this potential source material. Both of these materials will be evaluated and compared with residential soils.

2.2.2.1 On-smelter Facility Soils and Materials

As seen in Table 2.2.1, about five samples will be submitted for analysis from a single on-smelter facility location. Samples will be obtained from at least one site; however, if possible, samples will be obtained from all three near-by smelters (i.e., Globe, Omaha-Grant and Argo). For convenience the description of samples desired from nearby smelters will pertain to a single facility (Asarco). However, if samples from additional smelters are available, an attempt will be made to obtain the same quantities and types of samples as described for the Globe Plant. Desired samples are not limited to nearby smelters. Samples of arsenic trioxide from Asarco's Tacoma Plant in Tacoma, Washington will also be characterized, if available. Arsenic trioxide from the Tacoma Plant will be used to compare chemical attributes of residential soil from the VBI70 site (High, Intermediate, and Low), arsenic trioxide material collected from the Globe Plant, and the PAX sample.

All samples selected for analysis will have arsenic levels above 1000 ppm. Ideally, samples will be obtained from various locations about the site. The soils/materials of interest and their respective rationale for inclusion are provided below.

1) Soils with high arsenic concentrations that were collected near the arsenic kitchen(s) will be selected. Characterization of the on-smelter facility soils/materials containing high arsenic levels is key to determine if these soils/materials were transported in bulk to nearby residential soils.

2) Materials from inside of the stack will be selected. Characterization of the on-smelter facility materials that would have been deposited via air transport is important to determine if the residential soils were contaminated through air deposition.

3) Product, or by-product materials (e.g. arsenic trioxide product or materials from arsenic kitchens) will be selected. Characterization of the on-smelter facility materials that may have been used on residential properties either for fill material, as a soil amendment, or as an herbicide/pesticide; or in the

preparation of the herbicide PAX, is important to determine if these materials were transported in bulk to nearby residential soils.

A more in-depth description of the specific requirements of each sample type is provided below.

On-smelter Facility Soils
At least 3 soil sample locations will be identified for collection. Sample locations for on-smelter facility soils will be identified at regions where arsenic concentrations are above 1000 ppm. About 5 individual samples (sub-samples) that are within a 15-foot diameter of each other will be obtained. Ideally, arsenic concentrations of each sub-sample will be known and will be within 3 times the other 4 sub-samples selected for that location. However, if the concentration of each individual sub-sample is not known, 5 sub-samples will be collected in an area that is known to have soil levels above 1000 ppm.

A minimum of 170 grams (6 ounces) of soil must be submitted to the USEPA, Region 8 for soil testing. In areas where there is ample supply of sample, 240 g (8 oz) sample is best. However, if sufficient mass cannot be obtained for that sample, the USEPA contact (Bonnie Lavelle) will be reached for advice on how best to proceed.

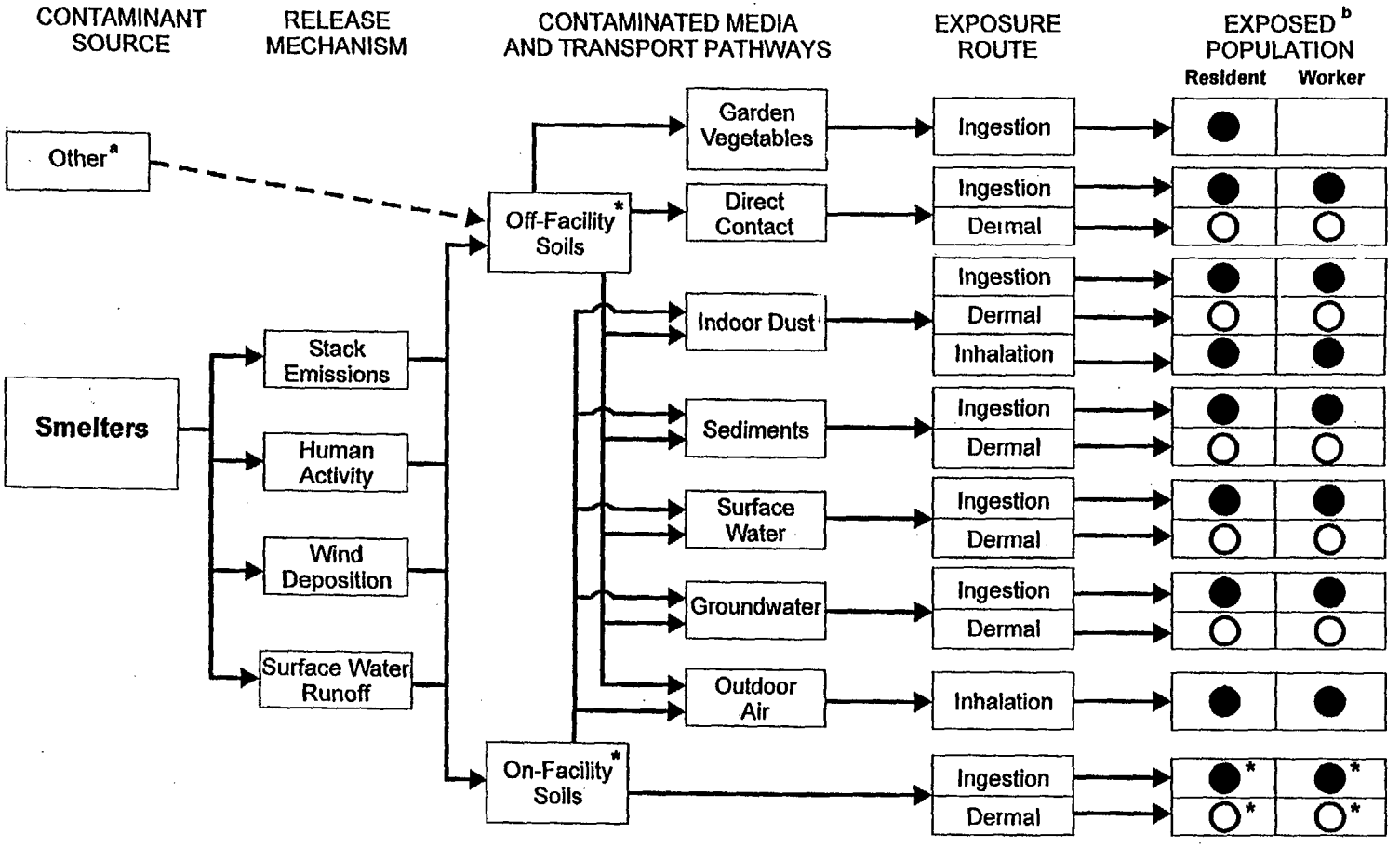
On-smelter Facility Materials
Each material obtained for testing will be measured in duplicate. Therefore, enough sample must be provided to support this. A minimum of 400 g (about 13 oz) of material must be submitted. However, if sufficient mass cannot be obtained for a sample, the USEPA contact (Bonnie Lavelle) will be reached for advice on how best to proceed.

2.2.2.2 PAX

PAX 3 Year Crabgrass Control (PAX) is an herbicide that was marketed between 1953 and 1974 for weed control on turf grass. The active ingredient of the PAX product is arsenic in the form of arsenic trioxide (25.11%) and lead arsenate (8.25%) (Hiltbold, 1973). Some have theorized that arsenic contained in the herbicide may remain in yards where PAX was applied. The USEPA has obtained a sample of PAX from the supplier which is now under chain-of-custody (Appendix B) and available for characterization.

Figure 2.2.9 Conceptual Site Model

Conceptual Site Model - Potential Human Exposure Pathways at Vasquez Blvd./I-70 Site (Revision 1)



= Pathway is not complete

= Pathway is complete, but minor; qualitative evaluation

= Pathway is complete and could be significant; quantitative evaluation

* "On-Facility" exposure is only at the former Omaha-Grant and Argo sites.

a- Other sources may be historical smelters, other active smelters & arsenical pesticides.

b- The work group will refine the list of exposed populations as the risk assessment proceeds and as additional site-specific data are obtained.

2.3 Soil Preparation

If soils collected from potential sources have not already been prepared (e.g., dried and sieved), a soil preparation step is required prior to analysis. After soil samples have been collected, they will be submitted under chain-of-custody for sample preparation.

Drying

Samples will be air-dried (not dried using heat) in a controlled environment prior to analysis. Soil dryness may be determined by performing a "squeeze" test. The soil plug is pinched between a freshly gloved thumb and index finger. If the soil fragments and becomes powdery, the sample may be regarded as adequately dry for sieving. Alternatively, if soil squeezed in the palm of a freshly gloved hand becomes cohesive and retains its shape after squeezing, the soil has too much moisture, and requires further drying.

If samples are not sufficiently dry, they should be air-dried by being allowed to stand in an open or partially covered sample container for 24 hours. Air-drying should be carried out in a warm room with moderate air circulation. If the soil is still too moist, it should be left to air dry for another 24 hours and tested again.

Rough guidelines for soil drying times are as follows:

- Sandy soil (24 hours)
- Silty soil (24 - 48 hours)
- Clayey soil (36 - 60 hours)

If samples are still not dry after these periods of air-drying, additional drying time may be necessary. Soils may not be dried in an oven.

Sieving

All samples should be field sieved (particle size < 2 mm) and should not be sieved further to the fine fraction (particle size < 250 μm) unless prescribed in the specified methodology (e.g., *in vitro* bioaccessibility).

Bulk Samples

In brief, all samples from the field (referred to as "raw" field samples) will be air-dried (as described above) and sieved to remove material larger than 2 mm using a #10 stainless steel sieve. The entire mass of each entire raw sample will be sieved in this way. Any material not passing through the 2 mm sieve will be disposed of as investigation derived waste (IDW). After sieving, the sample passing the sieve (now referred to as the "bulk" sample) is placed into a new zip-lock bag that is labeled with the original sample ID number, except that the suffix is "B" (for bulk) rather than "R" (for raw).

Fine Samples

Only as specified in the individual methods, bulk samples will be sieved a second time in order to isolate a fraction of fine particles for analysis. The fine sample is prepared by removing a portion of the bulk sample (about 10 g) and sieving through a #60 stainless steel sieve. After sieving, the material that does not pass through the screen is disposed of as IDW, and the material that does pass through the screen is placed into a new zip-lock bag labeled with the original sample ID number and the suffix "F" (for fine).

Decontamination

If disposable sieves or other equipment are not used during sample preparation, decontamination procedures must be performed before the tools or equipment may be reused.

2.4 Sample Nomenclature and Labeling

All samples collected during this study will be assigned a unique label ("tag number").

Each sample label will consist of three elements, as follows:

PHASE. All labels will begin with the letters "SC" to indicate that the sample is derived from the Soil Characterization Pilot Study.

NUMBER. Each label will include a unique identification number. This number will be a 5-digit sequential number starting with "00001" and progressively increasing until the final sample has been collected or tag number "99999" has been reached.

SAMPLE PREPARATION. Samples will be categorized based upon the sample preparation performed. Categories include, but are not limited to:

- R — Raw sample. Original sample collected during this study that is unprocessed.
- B — Bulk fraction. This sample has been prepared by sieving the sample to < 2 mm.
- F — Fine fraction. This sample has been prepared by sieving to < 250 μm.

Thus, "SC-00001-R" and "SC-12846-B" represent possible sample numbers collected during the pilot study.

Note: The sample preparation nomenclature may be expanded as needed in the future providing they are approved by the Project Database Manager or designate.

When a sample is collected (e.g., smelter soil or stack material), a self-adhesive label will be transferred from the pre-printed sheet to the sample container. At the same time (before collection of any other sample), the second copy of the sample number will be transferred to the appropriate location on the field data sheet. The sample data sheet will be filled out at the time of sample collection by the sample collection team. This sheet will contain all relevant information necessary to properly identify the sample. All data sheets will be maintained in three-ring binder logbooks.

2.5 Bulk Soil Characterization

Bulk soil characterization will be performed for all soil samples. A list of bulk soil characteristics that are believed to be useful for differentiation of soil types is provided in Table 2.5.1. A brief description of each method is provided below. All non-standard methods (i.e., all non-USEPA or non-Standard Methods references) referenced in the table are provided in Appendix A. Refer to these documents for procedural details.

Table 2.5.1 – Bulk Soil Characterization Parameter List

Bulk Soil Parameter	Method
Visual Inspection/Description (Qualitative Attributes)	Qualitative
Sand/Silt/Clay	ASTM D-2487
Soil pH	SW-846 9045C
Cation Exchange Capacity	SW-846 9080/9081
Total Organic Carbon	USEPA 9060
Particle Size Analysis	Gee & Bauder, 1986
Mineralogy of Sands, Silts, and Clays	XRD
Quantification of Perlite	Electron Microscopy

ASTM – American Society for Testing and Materials
XRD– X-ray Diffraction

Visual Inspection/Description (Qualitative Attributes). Soils will be visually inspected by a qualified geologist. Qualities such as color, homogeneity and geologic composition will be noted. In addition, the presence of non-geologic materials will be recorded.

Sand/Silt/Clay and Particle Size Analysis. Soil particles smaller that 2000 μm are generally divided into three major size groups: sands, silts and clays. Size class for soils will be defined using a standardized system of classification developed by the American Society for Testing and Materials (ASTM). In addition, perlite particle size and distribution will also be examined.

pH. The soil pH is measured by preparing a 1:1 saturated paste extract, which contains the test material and deionized water. This parameter defines the acidic or alkaline nature of the test soil.

Total Organic Carbon (TOC). This test determines the quantity of organic carbon present in a test soil. TOC is reported as mg TOC/kg soil.

Cation Exchange Capacity (CEC). CEC is defined as the capacity of soils to adsorb and exchange cations and it is related to the surface area and surface charge of the clay contained in the soils (Tan 1993). This test is commonly determined by extraction of the cations from soils with a solution containing a known cation for exchange. CEC is reported as the sum of milliequivalents of exchangeable cations per 100 g of soil.

Mineralogy of Sands, Silts, and Clays: This test employs use of x-ray diffraction (XRD) analysis to quantitatively classify soil into three standard soil classes: sands, silts, and clays. The sand and silt fractions will be analyzed using powder mounts, randomly oriented. Clay suspensions will be dried as thin films so that the plates are parallel to each other (preferred orientation). Specific mounting procedures are described in the mineralogy SOP (Appendix A).

Quantification of Perlite: This test will quantify the fraction of perlite observed in each soil or material by counting the occurrences observed using electron microscopy. The method used for this analysis is included in the metals speciation SOP (Appendix A), which utilizes the same instrumentation.

2.5.1 Data Use

The data collected from the bulk soil characterization tests will be used to compare individual bulk soil characteristics with other soils, as outlined in the table below.

Table 2.5.2 Data Use Comparisons for Bulk Soil Characteristics

Soil to be Compared	Residential Soil - Low	Residential Soil – Intermediate	Residential Soil - High
Residential Soil – Low	X	X	X
Residential Soil - Intermediate	X	--	X
Smelter Site Soil	X	X	X

-- Not Applicable

- Compare measured results of duplicate samples of each individual bulk soil parameter and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.5.2 Study Design Elements of PARCC for Bulk Soil Characterization

Each element of PARCC as it applies to evaluation of the bulk soil characterization is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples at a frequency of 10% of total samples (3 samples). Methods for evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting certified standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Representativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples with a wide range (high, intermediate, and low) of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible bulk soil characteristics. This approach should be representative for soils expected at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of the data points are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

2.6 Chemical Characteristics

The following chemical characteristics will measured as part of this pilot study:

- Metals concentrations (see Table 2.6.1 for complete analyte list)
- Geochemical Speciation (As, Pb, Cd, Zn, In, Tl, Hg, Se, Sb, and perlite)
- Stable Isotope Ratios of Lead
- Anion concentration (Chloride and Sulfate)
- *In Vitro* Bioaccessibility of Arsenic and Lead

Details pertaining to the particular chemical characteristic and its data uses are provided in the subsequent sections.

2.6.1 Metals Concentrations

All of the samples will be analyzed for a wide suite of metals (the Target Analyte List plus indium). This list is summarized in Table 2.6.1. The purpose is to see if there are any unique "fingerprint" metals or ratios of metals that can be used to distinguish on-facility site soils/materials from PAX and residential soils as well as between impacted and unimpacted residential soils. Mercury is included on the list despite the fact that the holding time requirements have been exceeded, because previous studies indicate that mercury is strongly correlated with the occurrence of arsenic in soils (see Appendix C). Indium will be also be quantified because this chemical has been observed at past investigations where Globe smelters activities were investigated (Drexler 1998).

Table 2.6.1 – Metals Target Analyte List

Target Analyte	PQLs[a] (ppm)	Method[b]
Aluminum	1	6010B or 7000 series
Antimony	1	
Arsenic	1	
Barium	0.5	
Beryllium	0.4	
Cadmium	1	
Calcium	1	
Chromium	0.5	
Cobalt	0.3	
Copper	1	
Iron	10	
Lead	1	
Magnesium	1	
Manganese	0.5	
Mercury [c]	0.2	
Nickel	0.5	
Potassium	100	
Selenium	1	
Silver	1	
Sodium	50	
Thallium	1	
Vanadium	0.5	
Zinc	1	
Indium	1	

PQL – Practical Quantitation Limit in units of mg/kg.
a - PQLs provided in this table are based upon 100% dry-weight.
b – SW-846 (USEPA 1986)
c – Method 7471A

2.6.1.1 Data Use

The data collected for the metals concentration analysis will be used to determine ratios of individual metals present in the soils and materials as outlined in the table below.

Table 2.6.2 Data Use Comparisons for Ratios of Individual Metals

Soil/Material to be Compared	Residential Soil – Low	Residential Soil - Intermediate	Residential Soil - High	Smelter Site Soil/Material
Residential Soil – Low	--	X	X	--
Residential Soil – Intermediate	X	--	X	--
Smelter Site Soil/Material	X	X	X	--
PAX	X	X	X	X

-- Not Applicable

- Compare measured results of duplicate samples of each individual metal concentration and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.6.1.2 Study Design Elements of PARCC for Metals Concentrations

Each element of PARCC as it applies to design and implementation of the metals concentration analysis is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples at a frequency of 10% of total samples (3 samples). Methods for evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting certified standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Representativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples that contain a wide range (high, intermediate, and low) of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible metals concentration ratios. This approach should be representative for all soils expected to be encountered at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of the data points are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

2.6.2 Geochemical Speciation

Information such as mineral phase, matrix association, particle size distribution, relative mass fraction, frequency of occurrence, density and concentration of metal in phase will be obtained through speciation. Each mineral phase describes the individual constituents of the soil and the proportion of each component. Matrix association can be referred to as "included" or "liberated". Mineral particles can either be enclosed within a matrix of rock or partly or entirely free of the rock. Enclosed particles are "included" and are essentially unavailable for adsorption. Free particles are "liberated" and may be more readily available for absorption, if ingested. Finally, particle size distribution per metal phase is important in determining which portion of the lead or arsenic mass is smallest. For example, small particles have high surface-to-area-to-volume ratio and are most likely to be readily dissolved or solubilized in the gastric fluids following ingestion.

The samples will be analyzed on a JEOL 8600 Superprobe located in the Department of Geological Science at the University of Colorado. The following elements will be included in this analysis: As, Pb, Cd, Zn, In, Tl, Hg, Sb, and Se. The six components used for speciatiation (particle length, matrix association, percent mass fraction, relative mass fraction, frequency of occurrence and liberation length), will be quantified and reported. Each sample will be examined for 8 hours and particle counts will be made for all target metals during this time period. For arsenic, the goal is to count 200 particles and the goal for lead is to count 100 particles. In the event that these goals are achieved in less than 8 hours, particle counting of Pb and As will be discontinued but counts of the other target metals (Cd, Zn, In, Tl, Se, Hg and Sb) will continue until the 8 hours has expired. Further details of the speciation methods to be used are available in the SOP (Appendix A).

2.6.2.1 Data Use

The data collected from the speciation analysis will be used to compare forms of target metals (As, Pb, Cd, Zn, In, Tl, Hg, Sb, Se) present in the soils and materials as outlined in the table as follows.

Table 2.6.3 Data Use Comparisons for Speciation Analysis

Soil/Material to be Compared	Residential Soil - Low	Residential Soil - Intermediate	Residential Soil - High	Smelter Site Soil/Material
Residential Soil – Low	--	X	X	--
Residential Soil – Intermediate	X	--	X	--
Smelter Site Soil/Material	X	X	X	--
PAX	X	X	X	X

- Compare measured speciation results of duplicate samples for each individual metal concentration and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.6.2.2 Study Design Elements of PARCC for Speciation Analysis

Each element of PARCC as it applies to design and implementation of the speciation analysis is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples for 3 sample locations, provided that a sufficient mass of sample is available. Methods for evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Represenatativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples that contain a wide (high, intermediate, and low) range of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible metals species. This approach should be representative for all soils expected to be encountered at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of data points required are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

2.6.3 Stable Isotope Ratios for Lead

Stable isotopes of lead exist in nature; however, analogous stable arsenic isotopes do not exist in nature. The ratio that each lead isotope is present in a soil or material is due primarily to the source of the lead. Since past investigations indicate that lead correlates with arsenic (see Appendix C), and because lead isotope ratios vary depending on the lead source, measurement of stable lead isotope ratio may be a diagnostic tool in source attribution. Therefore, stable lead isotope ratios will be determined in all soils and materials.

2.6.3.1 Data Use

The data collected from the laboratory tests will be used to calculate and compare lead isotope ratios in soils and materials, as outlined in the table below.

Table 2.6.4 Data Use Comparisons for Lead Isotope Ratios in Soils and Materials

Soil/Material to be Compared	Residential Soil - Low	Residential Soil – Intermediate	Residential Soil - High	Smelter Site Soil/Material
Residential Soil – Low	--	X	X	--
Residential Soil - Intermediate	X	--	X	--
Smelter Site Material	X	X	X	--
PAX	X	X	X	X

-- Not Applicable

- Compare measured isotope dilution results of duplicate samples for each individual metal concentration and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.6.3.2 Study Design Elements of PARCC for the Stable Isotope Ratios for Lead

Each element of PARCC as it applies to design and implementation of Stable Lead Isotope Ratio Analysis is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples for 10% of the soils (3 samples). Methods for evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting certified standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Representativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples that contain a wide range (high, intermediate, and low) of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible lead isotope ranges. This approach should be representative for all soils expected to be encountered at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of data points required are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

2.6.4 Anion Concentrations

All samples will be analyzed for chloride and sulfate, using the methods listed in Table 2.6.5. The purpose is to see if there are any unique "fingerprint" concentrations of chloride or sulfate that can be used to distinguish on-facility site soils/materials from PAX and residential soils, as well as between impacted and unimpacted residential soils.

Table 2.6.5 Anion Analyte List

Analyte	PQLs[a] (ppm)	Method[b]
Chloride	3	9056
Sulfate	6	

a -PQL – Practical Quantitation Limit in units of mg/kg.
b – SW-846 (USEPA 1986)

2.6.4.1 Data Use

The data collected for the anion concentration analysis will be used to compare individual concentrations of chloride and sulfate that are present in the soils and materials as outlined in the table as follows.

Table 2.6.6 Data Use Comparisons for Anion Concentration Analysis

Soil/Material to be Compared	Residential Soil - Low	Residential Soil – Intermediate	Residential Soil - High	Smelter Site Soil/Material
Residential Soil – Low	--	X	X	--
Residential Soil - Intermediate	X	--	X	--
Smelter Site Material	X	X	X	--
PAX	X	X	X	X

-- Not Applicable

- Compare measured anion concentration results of duplicate samples for each individual metal concentration and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.6.4.2 Study Design Elements of PARCC for Anion Concentrations

Each element of PARCC as it applies to design and implementation of the anion concentration analysis is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples at a frequency of 10% of total samples (3 samples). Methods for evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting certified standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Representativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples that contain a wide range (high, intermediate, and low) of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible anion concentrations. This approach should be representative for all soils expected to be encountered at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of the data points are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

2.6.5 *In Vitro* Bioaccessibility of Arsenic and Lead

The *In Vitro* Bioaccessibility Test will measure the percent of lead and arsenic solubilized under the specified test conditions. The *in vitro* bioaccessibility extractions and analysis will be performed according to SOP #A.6 attached in Appendix A.

2.6.5.1 Data Use

The data collected for the *in vitro* bioaccessibility analysis will be used to determine individual concentrations of lead and arsenic that are bioaccessible in the soils and materials as outlined in the table below.

Table 2.6.7 Data Use Comparisons for *In Vitro* Bioaccessibility Analysis

Soil/Material to be Compared	Residential Soil - Low	Residential Soil – Intermediate	Residential Soil - High	Smelter Site Soil/Material
Residential Soil – Low	--	X	X	--
Residential Soil - Intermediate	X	--	X	--
Smelter Site Material	X	X	X	--
PAX	X	X	X	X

-- Not Applicable

- Compare measured *in vitro* bioaccessibility results of duplicate samples for each individual metal concentration and quantify their agreement. This will be accomplished by plotting the original and duplicate samples and performing a linear regression analysis to evaluate the precision associated with each combined sampling and analysis methodology.

2.6.5.2 Study Design Elements of PARCC for the *In Vitro* Bioaccessibility Test

Each element of PARCC as it applies to design and implementation of the *in vitro* Bioaccessibility Test is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be determined by inserting duplicate or split samples for 3 sample locations. Methods for

evaluation of duplicate samples are outlined in Section 3.0.

Accuracy: Accuracy of the combined sampling and analysis procedures will be assessed by inserting standards samples into the analysis batch. Methods for evaluation of standards are outlined in Section 3.0.

Representativeness: As discussed in Section 2.1, representativeness is defined as the degree to which data accurately and precisely describe: 1) the overall sampled population (i.e., the site); or 2) the variability observed at a single sample location (i.e., variability due to temporal and/or seasonal changes). The first goal will be realized by measuring samples over at the low and high range of arsenic concentrations.

The limited sampling program is designed using a biased sampling scheme that stratifies samples across soil type (residential, on-smelter facility) and, therefore, presumably across possible solubility ranges. This approach should be representative for all soils expected to be encountered at VBI70. The second representativeness goal will not be addressed as part of this pilot-scale study.

Completeness: Requirements for overall project completeness is that 90% of data points required are collected and are valid.

Comparability: Comparability of data collected will be assured by requiring that all sampling and analysis procedures be followed in accordance with the SOPs.

3.0 Quality Assurance Project Plan

This section outlines the quality assurance/quality control (QA/QC) program required to ensure that the results of the study satisfy project requirements. This section summarizes the QA/QC program, which includes a system of procedures, checks, audits, and corrective actions to ensure that all technical, operational, monitoring, and reporting activities are of the highest achievable quality.

The surface soils that will be utilized for this project have already been collected and stored by USEPA under strict chain-of-custody procedures. Grab sample soils were collected at a depth interval of 0-2 inches.

3.1 Chain-of-Custody Forms

Sample custody history of each sample and its handling will be documented on a chain-of-custody (COC) form covering all transfers of custody until arrival at the analytical laboratory. The COC forms are completed by a member of the sampling team and are prepared in triplicate on carbonless forms. Each COC form will identify the samples included in the sample delivery group (SDG) and the required analyses. All corrections to the chain-of-custody record will be initialed and dated by the person making the corrections.

The following information should be included on each COC form:

Company Name
Address
Contact Name
Phone No. of Contact
Fax No.

A description of each field on the COC form and how it should be completed is provided below. Refer to Figure 3.1.1 for an example of a completed COC form.

Page -	Indicate page number and total number of COC pages in the SDG.
Proj. No.-	N/A
Project Name -	Enter the name of the project (VBI70 Pilot Scale Study).
Samplers(Signature) -	Sampler's name and signature.
Stat. No.	N/A
Date-	Enter the specific date the sample was collected.
Time-	Enter the specific time the sample was collected (24-hour time).
Comp.-	N/A
Grab-	Mark "X" in this column.
Station Location -	Note the discrete sample ID.
No. of Containers-	Mark "1" in this column.
(Blank)Analysis Required-	Indicate the method reference and name of analyses required. In the boxes below, mark an "X" to indicate the analysis is required for the respective sample ID.
Remarks-	Any notes of interest (sample condition, etc.) are entered here.
Relinquished by-	The person transferring the samples signs his name here.
Date/Time-	The person transferring the samples enters the date and time of relinquishment.
Received by-	The person accepting the samples signs his name here.
Date/Time-	The person accepting the samples enters the date and time of relinquishment.

U.S. ENVIRONMENTAL PROTECTION AGENCY
Environmental Services Division

CHAIN OF CUSTODY RECORD

REGION VIII, ONE DENVER PLACE
999 18TH. STREET
DENVER, CO. 80202-2413

PROJ. NO.	PROJECT NAME
	Vasquez Blvd. + I-70 Pilot-Scale Study

SAMPLERS: *(Signature)* John Doe

STAT. NO.	DATE	TIME	COMP.	GRAB	STATION LOCATION	NO. OF CONTAINERS	Bulk Soil Parameters (see attached)	Metals (ICP) (see list)	Mercury (CVAA)	Speciation (see list)	In Vitro Bioaccessibility	Pb stable Isotopes	REMARKS
—	5.29.99	—		X	SC-01234-B	1	X	X	X	X	X	X	Samples were field sieved
—	5.29.99	—		X	SC-56789-B	1	X	X	X	X	X	X	to < 2mm

John Doe 5.29.99

Relinquished by: *(Signature)*	Date/Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date/Time	Received by: *(Signature)*
John Doe	5.30.99 1705	Mary Goodside			
Relinquished by: *(Signature)*	Date/Time	Received by: *(Signature)*	Relinquished by: *(Signature)*	Date/Time	Received by: *(Signature)*
Relinquished by: *(Signature)*	Date/Time	Received for Laboratory by: *(Signature)*	Date/Time	Remarks	

Distribution: Original Accompanies Shipment: First Copy to Coordinator Field Files: Second Copy to Representative of Inspected Facility

Split Samples: ☐ Accepted ☐ Declined Signature

R8 EPA-014B (4-21-86)

Figure 3.1.1

8-31869

3.2 Laboratory Documentation

Contract Laboratory Program (CLP)-like data packages will be required for all laboratory analytical data. These CLP-like data packages will include a case narrative, copies of all associated raw data, sample results and all associated QC summaries. A summary of the data package requirements is shown as follows:

Section I **Case Narrative**

1. Case narrative
2. Copies of nonconformance/corrective action forms
3. Copies of sample receipt notices
4. Internal tracking documents, as applicable
5. Copies of all chain-of-custody forms

Section II **Analytical Results** - All results will be reported in units of mg/L or mg/kg.

1. Results for each parameter including dilutions and reanalysis
2. Units of measure
3. Practical Quantitation Limit
4. Date of sample analysis
5. Date of sample receipt
6. Date of sampling
7. Dilution factor

Section III **QA/QC Summaries**

1. Instrument blanks, initial calibration blanks, continuing calibration blanks, preparation (method) blanks and bottle blanks
2. Initial and continuing calibration verifications
3. Laboratory control samples
4. Matrix spikes
5. Method duplicates
6. Blank spikes
7. Instrument detection limits

Section IV **Instrument Raw Data** – Sequential measurement readout records for CVAA, GFAA, XRD, ICP, MS and XRD, which will include the following information:

1. Environmental samples, including dilutions and reanalyses
2. Initial calibration (including reporting the R-value for calibration line)
3. Initial and continuing calibration verifications
4. Instrument blanks, continuing calibration blanks, preparation (method) blanks and bottle blanks
5. Matrix spike
6. Method duplicates
7. Laboratory control samples

Section V **Other Raw Data**

1. Sample preparation logs
2. Instrument analysis logs for each instrument used
3. Standard preparation logs, including initial and final concentrations for each standard used

Section VI **Electronic Data** – All analytical data will be supplied in electronic form as well as hardcopy form. All data will be provided in ASCII format (comma or tab-delimited), that includes the required data fields, as specified in the Data Management Plan (Section 4.0). An example spreadsheet format has been developed and is attached (Figure 3.2.1).

FIGURE 3.2.1 Example of Database Format

ISSI Field Name	Field Name Definition	Data Type
Analysis Date CEC	Date of analysis for CEC	Bulk Soil Characterization
Analysis Date Mineralogy	Date of analysis for Mineralogy	Bulk Soil Characterization
Analysis Date Particle Size	Date of analysis for Particle Size	Bulk Soil Characterization
Analysis Date Perlite	Date of analysis for Perlite	Bulk Soil Characterization
Analysis Date Qualitative Attribut	Date of analysis for Qualitative Attributes	Bulk Soil Characterization
Analysis Date Sand/Silt/Clay	Date of analysis for Sand/Silt/Clay	Bulk Soil Characterization
Analysis Date Soil pH	Date of analysis for Soil pH	Bulk Soil Characterization
Analysis Date TOC	Date of analysis for TOC	Bulk Soil Characterization
Analysis Time CEC	Time of analysis for CEC	Bulk Soil Characterization
Analysis Time Mineralogy	Time of analysis for Mineralogy	Bulk Soil Characterization
Analysis Time Particle Size	Time of analysis for Particle Size	Bulk Soil Characterization
Analysis Time Perlite	Time of analysis for Perlite	Bulk Soil Characterization
Analysis Time Qualitative Attribu	Time of analysis for Qualitative Attributes	Bulk Soil Characterization
Analysis Time Sand/Silt/Clay	Time of analysis for Sand/Silt/Clay	Bulk Soil Characterization
Analysis Time Soil pH	Time of analysis for Soil pH	Bulk Soil Characterization
Analysis Time TOC	Time of analysis for TOC	Bulk Soil Characterization
Analyte CEC	Analyte result for CEC	Bulk Soil Characterization
Analyte Mineralogy	Analyte result for Mineralogy	Bulk Soil Characterization
Analyte Particle Size	Analyte result for Particle Size	Bulk Soil Characterization
Analyte Perlite	Analyte result for Perlite	Bulk Soil Characterization
Analyte Q CEC	Analyte qualifier for CEC	Bulk Soil Characterization
Analyte Q Mineralogy	Analyte qualifier for Mineralogy	Bulk Soil Characterization
Analyte Q Particle Size	Analyte qualifier for Particle Size	Bulk Soil Characterization
Analyte Q Perlite	Analyte qualifier for Perlite	Bulk Soil Characterization
Analyte Q Qualitative Attributes	Analyte qualifier for Qualitative Attributes	Bulk Soil Characterization
Analyte Q Sand/Silt/Clay	Analyte qualifier for Sand/Silt/Clay	Bulk Soil Characterization
Analyte Q Soil pH	Analyte qualifier for Soil pH	Bulk Soil Characterization
Analyte Q TOC	Analyte qualifier for TOC	Bulk Soil Characterization
Analyte Qualitative Attributes	Analyte result for Qualitative Attributes	Bulk Soil Characterization
Analyte Sand/Silt/Clay	Analyte result for Sand/Silt/Clay	Bulk Soil Characterization
Analyte Soil pH	Analyte result for Soil pH	Bulk Soil Characterization
Analyte TOC	Analyte result for TOC	Bulk Soil Characterization
Analytical Method CEC	Analytical Method for CEC	Bulk Soil Characterization
Analytical Method Mineralogy	Analytical Method for Mineralogy	Bulk Soil Characterization
Analytical Method Particle Size	Analytical Method for Particle Size	Bulk Soil Characterization
Analytical Method Perlite	Analytical Method for Perlite	Bulk Soil Characterization
Analytical Method Qualitative Att	Analytical Method for Qualitative Attributes	Bulk Soil Characterization
Analytical Method Sand/Silt/Clay	Analytical Method for Sand/Silt/Clay	Bulk Soil Characterization
Analytical Method Soil pH	Analytical Method for Soil pH	Bulk Soil Characterization
Analytical Method TOC	Analytical Method for TOC	Bulk Soil Characterization
Detection Limit CEC	Method detection limit for CEC	Bulk Soil Characterization
Detection Limit Mineralogy	Method detection limit for Mineralogy	Bulk Soil Characterization
Detection Limit Particle Size	Method detection limit for Particle Size	Bulk Soil Characterization
Detection Limit Perlite	Method detection limit for Perlite	Bulk Soil Characterization
Detection Limit Qualitative Attrib	Method detection limit for Qualitative Attributes	Bulk Soil Characterization
Detection Limit Sand/Silt/Clay	Method detection limit for Sand/Silt/Clay	Bulk Soil Characterization
Detection Limit Soil pH	Method detection limit for Soil pH	Bulk Soil Characterization
Detection Limit TOC	Method detection limit for TOC	Bulk Soil Characterization
Field ID	Full Field ID	Bulk Soil Characterization
Lab ID CEC	Laboratory Sample ID for CEC analysis	Bulk Soil Characterization
Lab ID Mineralogy	Laboratory Sample ID for Mineralogy analysis	Bulk Soil Characterization
Lab ID Particle Size	Laboratory Sample ID for Particle Size analysis	Bulk Soil Characterization
Lab ID Perlite	Laboratory Sample ID for Perlite analysis	Bulk Soil Characterization
Lab ID Qualitative Attributes	Laboratory Sample ID for Qualitative Attributes analysis	Bulk Soil Characterization
Lab ID Sand/Silt/Clay	Laboratory Sample ID for Sand/Silt/Clay analysis	Bulk Soil Characterization

ISSI Field Name	Field Name Definition	Data Type
Lab ID Soil pH	Laboratory Sample ID for Soil pH analysis	Bulk Soil Characterization
Lab ID TOC	Laboratory Sample ID for TOC analysis	Bulk Soil Characterization
Preparation Method No CEC	Preparation Method Reference for CEC	Bulk Soil Characterization
Preparation Method No Mineralo	Preparation Method Reference for Mineralogy	Bulk Soil Characterization
Preparation Method No Particle	Preparation Method Reference for Particle Size	Bulk Soil Characterization
Preparation Method No Perlite	Preparation Method Reference for Perlite	Bulk Soil Characterization
Preparation Method No Qualitati	Preparation Method Reference for Qualitative Attributes	Bulk Soil Characterization
Preparation Method No Sand/Sil	Preparation Method Reference for Sand/Silt/Clay	Bulk Soil Characterization
Preparation Method No Soil pH	Preparation Method Reference for Soil pH	Bulk Soil Characterization
Preparation Method No TOC	Preparation Method Reference for TOC	Bulk Soil Characterization
Units CEC	Units of measure for CEC	Bulk Soil Characterization
Units Mineralogy	Units of measure for Mineralogy	Bulk Soil Characterization
Units Particle Size	Units of measure for Particle Size	Bulk Soil Characterization
Units Perlite	Units of measure for Perlite	Bulk Soil Characterization
Units Qualitative Attributes	Units of measure for Qualitative Attributes	Bulk Soil Characterization
Units Sand/Silt/Clay	Units of measure for Sand/Silt/Clay	Bulk Soil Characterization
Units Soil pH	Units of measure for Soil pH	Bulk Soil Characterization
Units TOC	Units of measure for TOC	Bulk Soil Characterization
COC No	Chain-of-Custody Number	COC
Comp/Grab	Sample type: composite or grab sample	COC
Field ID	Full Field ID	COC
Sample Date	Date sampled in the field	COC
Sample Time	Time sampled in the field	COC
Field ID	Full Field ID	Field Collection
Old Field ID	North Denver Field ID	Field Collection
Sample Type	Distinguishes between field and QC samples (e.g. field, duplicate)	Field Collection
As Extract Conc	Extract Concentration of As (µg/L)	In Vitro Bioaccessibility
Bulk As Conc.	Bulk Concentration of As (mg/Kg dry weight)	In Vitro Bioaccessibility
Bulk Pb Conc.	Bulk Concentration of Pb (mg/Kg dry weight)	In Vitro Bioaccessibility
Pb Extract Conc	Extract Concentration of Pb (µg/L)	In Vitro Bioaccessibility
Analysis Date Metal	Date of analysis for Metal (Repeat for each of 23 metals)	Metal Concentration
Analysis Date Pb204	Date of analysis for Pb204	Metal Concentration
Analysis Date Pb206	Date of analysis for Pb206	Metal Concentration
Analysis Date Pb207	Date of analysis for Pb207	Metal Concentration
Analysis Date Pb208	Date of analysis for Pb208	Metal Concentration
Analysis Time Metal	Time of analysis for Metal (Repeat for each of 23 metals)	Metal Concentration
Analysis Time Pb204	Time of analysis for Pb204	Metal Concentration
Analysis Time Pb206	Time of analysis for Pb206	Metal Concentration
Analysis Time Pb207	Time of analysis for Pb207	Metal Concentration
Analysis Time Pb208	Time of analysis for Pb208	Metal Concentration
Analyte Metal	Analyte result for Metal (Repeat for each of 23 metals)	Metal Concentration
Analyte Pb204	Analyte result for Pb204	Metal Concentration
Analyte Pb206	Analyte result for Pb206	Metal Concentration
Analyte Pb207	Analyte result for Pb207	Metal Concentration
Analyte Pb208	Analyte result for Pb208	Metal Concentration
Analyte Q Metal	Analyte qualifier for Metal (Repeat for each of 23 metals)	Metal Concentration
Analyte Q Pb204	Analyte qualifier for Pb204	Metal Concentration
Analyte Q Pb206	Analyte qualifier for Pb206	Metal Concentration
Analyte Q Pb207	Analyte qualifier for Pb207	Metal Concentration
Analyte Q Pb208	Analyte qualifier for Pb208	Metal Concentration
Analytical Method Metal	Analytical Method for Metal (Repeat for each of 23 metals)	Metal Concentration
Analytical Method Pb204	Analytical Method for Pb204	Metal Concentration
Analytical Method Pb206	Analytical Method for Pb206	Metal Concentration
Analytical Method Pb207	Analytical Method for Pb207	Metal Concentration
Analytical Method Pb208	Analytical Method for Pb208	Metal Concentration
Detection Limit Metal	Method detection limit for Metal (Repeat for each of 23 metals)	Metal Concentration
Detection Limit Pb204	Method detection limit for Pb204	Metal Concentration

ISSI Field Name	Field Name Definition	Data Type
Detection Limit Pb206	Method detection limit for Pb206	Metal Concentration
Detection Limit Pb207	Method detection limit for Pb207	Metal Concentration
Detection Limit Pb208	Method detection limit for Pb208	Metal Concentration
Lab ID Metal	Laboratory Sample ID for Metal (Repeat for each of 23 metals) analysis	Metal Concentration
Lab ID Pb204	Laboratory Sample ID for Pb204 analysis	Metal Concentration
Lab ID Pb206	Laboratory Sample ID for Pb206 analysis	Metal Concentration
Lab ID Pb207	Laboratory Sample ID for Pb207 analysis	Metal Concentration
Lab ID Pb208	Laboratory Sample ID for Pb208 analysis	Metal Concentration
Preparation Method No Metal	Preparation Method Reference for Metal (Repeat for each of 23 metals)	Metal Concentration
Preparation Method No Pb204	Preparation Method Reference for Pb204	Metal Concentration
Preparation Method No Pb206	Preparation Method Reference for Pb206	Metal Concentration
Preparation Method No Pb207	Preparation Method Reference for Pb207	Metal Concentration
Preparation Method No Pb208	Preparation Method Reference for Pb208	Metal Concentration
Units Metal	Units of measure for Metal (Repeat for each of 23 metals)	Metal Concentration
Units Pb204	Units of measure for Pb204	Metal Concentration
Units Pb206	Units of measure for Pb206	Metal Concentration
Units Pb207	Units of measure for Pb207	Metal Concentration
Units Pb208	Units of measure for Pb208	Metal Concentration
Analysis Date As Speciation	Date of analysis for As Speciation	Speciation
Analysis Date Pb Speciation	Date of analysis for Pb Speciation	Speciation
Analysis Date Cd Speciation	Date of analysis for Cd Speciation	Speciation
Analysis Date Zn Speciation	Date of analysis for Zn Speciation	Speciation
Analysis Date In Speciation	Date of analysis for In Speciation	Speciation
Analysis Date Tl Speciation	Date of analysis for Tl Speciation	Speciation
Analysis Date Hg Speciation	Date of analysis for Hg Speciation	Speciation
Analysis Date Se Speciation	Date of analysis for Se Speciation	Speciation
Analysis Date Sb Speciation	Date of analysis for Sb Speciation	Speciation
Analysis Time As Speciation	Time of analysis for As Speciation	Speciation
Analysis Time Pb Speciation	Time of analysis for Pb Speciation	Speciation
Analysis Time Cd Speciation	Time of analysis for Cd Speciation	Speciation
Analysis Time Zn Speciation	Time of analysis for Zn Speciation	Speciation
Analysis Time In Speciation	Time of analysis for In Speciation	Speciation
Analysis Time Tl Speciation	Time of analysis for Tl Speciation	Speciation
Analysis Time Hg Speciation	Time of analysis for Hg Speciation	Speciation
Analysis Time Se Speciation	Time of analysis for Se Speciation	Speciation
Analysis Time Sb Speciation	Time of analysis for Sb Speciation	Speciation
Analytical Method As Speciation	Analytical Method for As Speciation	Speciation
Analytical Method Pb Speciation	Analytical Method for Pb Speciation	Speciation
Density As	Density As of the phase	Speciation
Density Pb	Density Pb of the phase	Speciation
Fraction As	Fraction of the material that is comprised of As	Speciation
Fraction Pb	Fraction of the material that is comprised of Pb	Speciation
Lab ID As Speciation	Laboratory Sample ID for As Speciation analysis	Speciation
Lab ID Pb Speciation	Laboratory Sample ID for Pb Speciation analysis	Speciation
Length As	Particle Length for each As phase	Speciation
Length Pb	Particle Length for each Pb phase	Speciation
Lib Length As	Maximum Length of the Liberated form of As phase	Speciation
Lib Length Pb	Maximum Length of the Liberated form of Pb phase	Speciation
Lib? As	Identifies whether As phase is liberated form or not liberated form	Speciation
Lib? Pb	Identifies whether Pb phase is liberated form or not liberated form	Speciation
Mineral As Speciation	Mineral Name for As	Speciation
Mineral Pb Speciation	Mineral Name for Pb	Speciation
Preparation Method No As Spec	Preparation Method Reference for As Speciation	Speciation
Preparation Method No Pb Spec	Preparation Method Reference for Pb Speciation	Speciation
Units As Speciation	Units of measure for As Speciation	Speciation
Units Pb Speciation	Units of measure for Pb Speciation	Speciation

3.3 Sample Handling and Shipping

Sample handling protocols are important to establish and maintain the integrity of all samples from collection to analysis. The appropriate sampling media shall be collected using the methods prescribed in the SOPs. After collection, the samples must be prepared for shipment and immediately sent to the analytical laboratory prior to expiration of analytical holding times. Strict chain-of-custody and shipping procedures must be observed.

3.3.1 Shipping Procedures

Soil samples may be shipped to the laboratory at ambient temperatures in International Air Transport Association (IATA) approved packaging. Shipment of environmental samples is excluded as hazardous waste; therefore no special labeling or handling is required.

3.3.2 Chain-of-Custody Procedures

Chain-of-custody is defined as an unbroken trail of accountability that ensures the physical security of samples, data, and records. These procedures are employed to ensure that samples are properly tracked and maintained from collection to disposal. All samples collected in the field will be submitted to the appropriate analytical laboratory under chain-of-custody. A sample is considered to be in one's custody if:

- the sample is physically in that one's possession;
- the sample is in that one's view, after being in that one's physical possession;
- the sample is locked on the premises or otherwise sealed so that tampering will be evident, after being in that one's physical possession; or
- the sample is kept in a secure and restricted area, after being in one's physical possession.

All sample transfers must adhere to chain-of-custody procedures detailed below. Each complete COC form will be reviewed for accuracy and clarity by the shipper. When the samples are handed over to a designated lab courier, the courier will compare sample inventory with the COC form to ensure accuracy. The COC forms are then signed by the courier to serve as written acknowledgment that the samples have been transferred intact to the courier. The sampler will be given a copy of the COC form with release signatures. One copy of the COC form will be retained by the shipper. When the samples arrive at the laboratory, the lab's sample custodian will document the date and time of receipts and condition of the samples (temperature of samples, note any damage, etc.).

Third party custody will be required when samples are shipped. Third parties include shipping companies such as FedEx, UPS and USPS. Samples will be shipped overnight in tightly sealed ice chests. All packing procedures will conform to appropriate IATA

and/or DOT requirements as described in Section 3.3.1. Often, third party couriers or clerks will not sign for relinquishment on COC forms. Instead, copies of the shipping/tracking forms will be retained as documentation of transfer of custody. The COC form which corresponds to the samples being shipped will be sealed inside the shipping container, inside a plastic zip-lock bag and taped to the cooler lid to avoid water damage from ice.

3.4 Quality Control Requirements

The principle objectives of any sampling and analysis program are to obtain accurate and representative environmental samples and to provide valid analytical data. The quality of data will be assessed through the use of QC samples performed on a regular basis. Laboratory QC samples will be analyzed as per analytical method protocols to evaluate whether laboratory procedures and analyses have been completed properly. For this project, the types of QC samples to be analyzed are defined and their role in the production of QC data are discussed in the following sections. In addition to the particular QC requirements identified in the subsequent sections, all analyses must be performed within specified holding times and must adhere to all procedures as outlined in the appropriate SOPs (Appendix A). The following sections describe the quality control samples required for this study. Acceptance criteria and corrective action procedures are also summarized in Tables 3.7.2, 3.7.3 and in the attached SOPs (Appendix A).

3.4.1 Blind Quality Control Samples

Blind Field Duplicate/Split Samples: Blind field duplicate and blind field split samples are two aliquots of the same sample that have been prepared blind to the analyst only after the original sample has been properly prepared (oven-dried, sieved and homogenized). These samples are submitted blind by the field sample preparation technician to the field or contract laboratory to measure the precision of laboratory preparation and analysis. If field duplicates have been collected for any of the samples identified for evaluation, these samples will be submitted for duplicate analysis. A maximum of 3 field duplicates are required for each analysis, provided that sufficient sample mass is available. In the event that field duplicates are not available, up to 3 split samples will be prepared. Split samples are prepared by ensuring the sample is well-mixed and then divided into two. The split samples are containerized and labeled like all other samples and submitted blind to the laboratory to test the precision of the laboratory analysis and sample splitting and the precision of sample collection. Metals concentration, and all smelter material analyses must have sample splits available to verify the precision of each measurement. If sufficient sample material is available, all chemical and physical tests should have at least 3 splits inserted into the sample stream.

The RPD for blind field splits should not exceed 25% or, alternatively, the absolute difference should not exceed 1 x MDL. However, these acceptance limits may be arbitrary; therefore, a graphical comparison of the original and field split samples should also be prepared. This comparison will include a linear regression and will report the calculated correlation coefficient (r). Additionally, control charting will be performed in

accord with standard USEPA protocols and will be used to establish site-specific performance criteria for field split samples.

Blind Standard: The accuracy of an analytical method is evaluated by analyzing a sample medium fortified with a known concentration of target analytes that has been certified using the preparation and analysis method for that particular sample medium. This sample is submitted to the field or contract laboratory blind at a frequency of about 10% (about 3 samples) for each level. The accuracy requirements will be provided by the certifying laboratory. Recoveries will also be monitored using control charting. Control charting will be performed in accord with standard USEPA protocols and will be used to establish site-specific performance criteria. These samples will be analyzed in both the field laboratory and contract laboratory. Blind standards will be provided for metals and anions concentrations only.

Equipment Blank: An equipment blank is a collection of the rinsate produced from rinsing equipment that has been decontaminated after use with 100-120 mLs of analyte-free deionized water. Equipment blanks must be performed at a frequency of 5% of all decontaminations performed on each type of equipment. Concentrations of target analytes greater than 1 x MDL for most analytes and 5-10 x MDL for laboratory-induced contaminants may suggest that field sampling-induced contamination may have occurred. This sample will only be collected by personnel if decontamination is required. If all preparation equipment is disposable (one-use only), then equipment blanks are not collected.

3.4.2 Laboratory Quality Control Samples

Matrix Spike: The accuracy of an analytical method is evaluated by analyzing a sample medium fortified with a known concentration of target analytes. A matrix spike is the analysis of a known concentration of target analytes added to the sampling medium. Matrix spikes will be prepared for metals concentration analysis only. A matrix spike will be performed at a frequency of 5% (1 matrix spike for every 20 samples) for all chemical analyses. Matrix spike results must be within 75-125% of the known value.

Instrument Blank: An instrument blank is composed of the sample matrix for the investigative samples prepared for analysis. For example, instrument blanks are composed of the same nitric acid reagent used for metals analyses performed by method 6010B. Instrument blanks are analyzed to discern if laboratory-induced contamination is present during analysis and must be performed at a frequency of 5% of samples (1 method blank per 20 samples analyzed or 1 method blank per extraction batch) on all chemical analyses. Concentrations of target analytes must not exceed 1 x MDL.

Laboratory Control Samples (LCS): A LCS originates in the laboratory or is provided as a standard reference material (SRM) by a manufacturer (eg. NIST) and contains target analytes of known concentration. Because LCSs are independent of the calibration standards, they are analyzed to verify the accuracy of the standards used to calibrate the instrument. At least one LCS must be analyzed in each analysis batch.

Laboratory Duplicates: Laboratory duplicates are samples that are split at the laboratory. These samples are prepared with all other samples at the laboratory and measure the precision of the laboratory preparation and analysis. Laboratory duplicates must be performed at a frequency of 5% of samples (1 method duplicate per 20 samples digested) except for the *in vitro* bioaccessibility method. The frequency for laboratory duplicates for the *in vitro* bioaccessibility method is 10% (1 method duplicate per 10 samples).

Method Blank: A method blank is composed of the sample matrix for the investigative samples prepared for analysis and is prepared as an investigative sample. Method blanks are analyzed to discern if laboratory-induced contamination is present during analysis and must be performed at a frequency of 5% of samples (1 method blank per 20 samples analyzed or 1 method blank per extraction batch) on all chemical analyses. Concentrations of target analytes must not exceed 1 x MDL.

Bottle blank: A bottle blank consists of extraction fluid (no test material) that is taken through the complete *in vitro* bioaccessibility extraction procedure. Arsenic and lead in this sample must be below the MDL.

Blank spike: A blank spike consists of extraction fluid spiked at 10 mg/L lead and 1 mg/L arsenic (use traceable 1000 mg/L lead and arsenic standards for making spikes) that is run through the complete *in vitro* bioaccessibility extraction procedure at a frequency of 1 in 20 samples. Calculated percent recoveries for arsenic and lead should fall within the range of 85-115%.

3.4.3 Detection Limits

MDLs are defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the true value is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. A MDL study must be performed for each method utilized in the study in accord with guidance outlined in the 40 CFR Part 136, Appendix B.

The PQL is defined as 10 times the standard deviation determined from the MDL study (or often described as 3 times the MDL). The PQLs required for each analytical methodology planned for this investigation are summarized in Table 2.6.1.

3.4.4 QA/QC Elements of PARCC

Each element of PARCC as it applies to QA/QC procedures is provided in this section.

Precision: Precision of the combined sampling and analysis procedure will be measured by measuring field duplicate and/or split samples. This will be accomplished by plotting the original and field duplicate samples and performing a linear regression analysis. The calculated coefficient (R) should be >0.9.

Accuracy: For a variety of analytical procedures, standard reference materials traceable to or available from National Institute of Standards and Technology (NIST) or other sources can be used to determine accuracy of measurements. Accuracy will be measured as the percent recovery (%R) , which is calculated as follows:

$$\%R = \frac{A}{B} \times 100\%$$

Where:

A = measured concentration value of an analyte
B = certified concentration value of an analyte

The percent recovery for the blind standard, the blank spike and the laboratory control samples are defined in each standard USEPA protocol or SOP (Appendix A).

Representativeness: Analytical methodologies identified for this investigation have been chosen to measure chemicals that are representative of the chemical mixtures present in soil.

Completeness: Data produced by an analytical laboratory must be valid for at least 90% of analyzed samples. This means that fewer than 10% of all analytical data generated for each analysis method may incur a qualification of unusable (R qualification). If this completeness goal is not met, the analytical laboratory responsible for generating the poor quality data must reanalyze samples without additional cost and reanalyses must adhere to method requirements to generate valid data.

Comparability: Comparability will be achieved by analyzing samples using standardized methodologies. All data produced as part of this investigation must have followed the procedures outlined in this project plan.

3.5 Instrument/Equipment Testing, Inspection and Maintenance Requirements

Laboratory equipment planned for chemical or physical analysis during this investigation must be inspected daily to ensure it remains in good working condition. Any maintenance that is performed on the instruments must be documented in the respective instrument maintenance logbook.

3.6 Instrument Calibration Frequency

Laboratory instrumentation, used for sample analyses, will be calibrated in accordance with the standard USEPA protocols or SOPs (Appendix A). Calibrations must be acceptable before any measurements may be made. Calibration procedures and frequencies are summarized in Appendix A. Traceable calibration standards will be obtained by the analytical laboratories. All documentation relating to the receipt, preparation and use of standards will be recorded in the appropriate laboratory logbooks.

3.7 Assessment and Oversight

The following sections describe activities for assessing the effectiveness of the implementation of the project and associated quality assurance/quality control (QA/QC). The purpose of the assessment is to ensure that the project plan is implemented as prescribed. The elements include assessments and response actions and reports to management as described in the following sections.

3.7.1 Assessment and Response Actions

Laboratory Audits

Assessment of laboratory analyses will be conducted through oversight of analytical procedures, through optional laboratory audits and/or through submittal of performance evaluation samples. The purpose of the oversight activities will be to document analytical procedures including changes, additions or deletions that occurred during analysis. If any procedures do not meet project requirements, then corrective action for the deviation must be requested, reviewed and reported. Laboratory audits will evaluate laboratory procedures to ensure that they follow GLP (Good Laboratory Practices) Guidelines and to ensure that they do not conflict with project requirements. If conflicts are noted, these must be addressed so that project requirements are met.

Performance evaluation (PE) samples may be used as a tool for evaluating the accuracy of laboratory analyses. PE samples are standards submitted blind to the laboratory and are typically submitted prior to submittal of investigative samples, but may also be inserted blindly into the sample stream. The concentration is unknown to the laboratory analyzing the sample, but known to the submitter. The laboratory reported results for the PE samples will be evaluated by comparison to the certified values provided to USEPA Region 8 or its designate by the PE sample vendor. Acceptance criteria in terms of percent recovery windows may be established as appropriate to determine comparability. The degree of comparability expected between the certified values and the laboratory reported results will depend on a number of factors, including the accuracy and precision reported by the vendor for the certified values and the comparability of the certification analysis method used by the vendor with the analysis methods used by the laboratory.

3.7.2 Corrective Action Procedures

Two types of corrective actions may result from audits and/or oversight: immediate and long-term. Immediate corrective actions include correcting deficiencies or errors or correcting inadequate procedures. Long-term corrective actions are designed to eliminate the sources of deficiencies or errors. If either type of corrective action is deemed necessary following an audit, each step in the following procedures must be documented:

1) Identify the deviation
2) Request a corrective action
3) Report the problem the USEPA RPM
4) Review the corrective action response
5) Perform a follow-up audit to ensure the deviation is not recurring

Appropriate corrective action procedures for specific laboratory or field quality control samples are outlined in the subsequent paragraphs. Refer to Tables 3.7.2 and 3.7.3 for recommended corrective actions for metals and anions analyses. Refer to SOP #A.7 for recommended corrective actions for *in vitro* bioaccessibility analysis.

Table 3.7.2: QC Requirements and Recommended Corrective Action for Metals

QC Performed	Minimum Frequency	Acceptance Criteria					Recommended Corrective Action				
		General Requirements (GR) *	GFAA Method 7060 & 7421	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A	General Requirements (GR)	GFAA Method 7000	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A
Field Duplicate (FD) / Field Splits	If field duplicates have been collected for any of the samples identified for evaluation, they will be submitted. In the event that field duplicates are not available, up to 3 split samples will be prepared for each analysis	RPD < 25% or,the absolute difference should not exceed 1 x MDL. A graphical comparison of the original and field duplicate samples should also be prepared. Recoveries will also be monitored using control charting. Control charting will be performed in accord with standard USEPA protocols and will be used to establish site-specific performance criteria. This comparison will include a linear regression and will report the calculated correlation coefficient. R should be >0.9.	See GR	See GR	See GR	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples are factors in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-extract or redigest and reanalyze the method duplicate and associated investigative samples.*	See GR	See GR	See GR	See GR
Blind Standard	10% of all surface soil samples.	Accuracy requirements will be provided by the certifying laboratory. Recoveries will also be monitored using control charting. Control charting will be performed in accord with standard USEPA protocols and will be used to establish site-specific performance criteria.	See GR	See GR	See GR	See GR	Verify the percent recovery calculations. If calculations are correct, the RPM will request the analyst to reanalyze the sample. If reanalysis results are still outside of acceptance limits, submit another blind standard immediately into the sample stream to determine if the analysis shows a trend or an isolated event. *Analysis of site samples may be discontinued until the problem is resolved.*	See GR	See GR	See GR	See GR
Blind Field Split (BS)/ Blind Field Duplicate	5% of all surface soil samples (1 field duplicate per 20)	RPD < 25% or,the absolute difference should not exceed 1 x MDL. A graphical comparison of the original and field duplicate samples should also be prepared. Recoveries will also be monitored using control charting. This comparison will include a linear regression and will report the calculated correlation coefficient. R should be >0.9. Additionally, control charting will be performed in accord with standard USEPA protocols and will be used to establish site-specific performance criteria.	See GR	See GR	See GR	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples are factors in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-extract or redigest and reanalyze the method duplicate and associated investigative samples.*	See GR	See GR	See GR	See GR

Table 3.7.2: QC Requirements and Recommended Corrective Action for Metals

QC Performed	Minimum Frequency	Acceptance Criteria					Recommended Corrective Action				
		General Requirements (GR) *	GFAA Method 7060 & 7421	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A	General Requirements (GR)	GFAA Method 7000	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A
Matrix Spike (MS)	5% or 1 per batch (whichever is more frequent)	N/A	80-120% recovery of known value	75-125% spiked sample recovery (spiking level plus original sample level)	75-125% recovery of known value	75-125% recovery of known value	Verify the matrix spike percent recovery calculations and evaluate the LCS percent recoveries. If the calculations are correct and the LCS recoveries are acceptable, determine if matrix interference is a factor in the poor recoveries. If matrix effects are not observed, reanalyze the matrix spike and associated investigative samples. *If appropriate, re-extract or redigest and reanalyze the matrix spike and associated investigative samples.*	Interference test must be conducted (see SW 846 Method 7060 and 7421 for description of interference tests).	Locate source of the problem, correct it, and re-analyze any samples that were run during the out-of-control condition.	Locate source of the problem, correct it, and re-analyze any samples that were run during the out-of-control condition.	Interference test must be conducted (see SW 846 Method 7060 and 7421 for description of interference tests).
Post-digestion Spike (PDS)	as required; if matrix spike does not meet acceptance criteria	N/A	85-115% of known value	85-115% recovery of post spiked sample	75-125% of known value.		Verify the percent recovery calculations. If these are acceptable and the spike addition produces a minimum level of 10 times to a maximum of 100 times the instrument detection limit (IDL), matrix effects should be suspected. No further action is required.	If recovery <40%, dilute sample by factor of 5-10 and rerun. If after dilution recovery still <40%, report problem to USEPA.	Sample must be diluted and re-analyzed to compensate for possible matrix effects. Results must agree to within 10% of the original determination.	Sample must be diluted and re-analyzed to compensate for possible matrix effects. Results must agree to within 10% of the original determination	If recovery <40%, dilute sample by factor of 5-10 and rerun. If after dilution recovery still <40%, report problem to USEPA.
Laboratory Control Sample (LCS) or Standard Reference Material (SRM)	5% or 1 per batch (whichever is more frequent)	must be within manufacturer's established acceptance limits	80-120% of known value	See GR	See GR	See GR	Verify the percent recovery calculations. Evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the LCS and associated investigative samples. If necessary, recalibrate the instrument. *Do not continue analysis until the problem is solved.*	Re-run the LCS or SRM one time, if still not acceptable, all samples analyzed after the last acceptable LCS must be re-prepped and re-analyzed.	See GR	See GR	Re-run the LCS or SRM one time, if still not acceptable, all samples analyzed after the last acceptable LCS must be re-prepped and re-analyzed
Method Duplicate (MD)	5% or 1 per batch (whichever is more frequent)	RPD < 25% (if 5 x MDL), absolute difference 1 x MDL	See GR	RPD < 25% (if 5 x MDL), absolute difference 1 x MDL	RPD < 25% (if 5 x MDL), absolute difference 1 x MDL	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples is a factor in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-extract or redigest and reanalyze the method duplicate and associated investigative samples.*	See GR	See GR	See GR	See GR

Table 3.7.2: QC Requirements and Recommended Corrective Action for Metals

QC Performed	Minimum Frequency	Acceptance Criteria					Recommended Corrective Action				
		General Requirements (GR) *	GFAA Method 7060 & 7421	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A	General Requirements (GR)	GFAA Method 7000	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A
Initial Calibration Verification (ICV)	beginning of each run *and end, after the last analytical sample*; or beginning of every new shift (whichever is more frequent)(after the ICB)	N/A	90-110% recovery of known value	90-110% recovery of known value	90-110% recovery of known value	A calibration curve must be prepared each day, with a minimum of 3 standards and one blank. After calibration, the calibration curve must be verified by the use of an ICB and ICV. Recovery of the ICV must be 90-110% of known value.	Verify the percent recovery calculations. If calculations are correct, evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the ICV and all associated investigative samples. If necessary, recalibrate the instrument. *Do not continue analysis until the problem is solved.*	Calibration curves must cover the appropriate concentration range, as determined by Project specifications. Blanks and standards should produce an absorbance of 0.0 - 0.7	Terminate analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be re-analyzed.	Terminate analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be re-analyzed.	Calibration curves must cover the appropriate concentration range, as determined by Project specifications. Blanks and standards should produce an absorbance of 0.0 - 0.7
Initial Calibration Blank (ICB)	beginning of each run or beginning of every new shift (whichever is more frequent)(before the ICV)	N/A	≤ 1 x MDL	< 1 x MDL	< 3 x IDL for each analyte.	≤ 1 x MDL	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meets acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	Determine the cause, correct the problem, and recalibrate the instrument before any samples are analyzed.	See GR	See GR	Determine the cause, correct the problem, and recalibrate the instrument before any samples are analyzed.
Continuing Calibration Verification (CCV)	every 10 samples in the analytical batch (after the CCB) For XRF analyses, once per batch of investigative samples.	N/A	90-110% recovery of known value	90-110% recovery of known value	90-110% recovery of known value	80-120% of known value	Verify the percent recovery calculations. If calculations are correct, evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the CCV and all associated investigative samples. If necessary, recalibrate the instrument. *Do not continue analysis until the problem is solved. If std > control limits, stop analysis, correct problem, recalibrate instrument, verify calibration, and reanalyze all samples analyzed since the last good CCV.*	Discontinue sample analysis, determine cause of the problem, correct the problem, and recalibrate the instrument.	See GR	See GR	Discontinue sample analysis, determine cause of the problem, correct the problem, and recalibrate the instrument.

Table 3.7.2: QC Requirements and Recommended Corrective Action for Metals

QC Performed	Minimum Frequency	Acceptance Criteria					Recommended Corrective Action				
		General Requirements (GR) *	GFAA Method 7060 & 7421	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A	General Requirements (GR)	GFAA Method 7000	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A
Continuing Calibration Blank (CCB)	every 10 samples in the analytical batch (before the CCV), *or once every 2 hrs during the analytical run, whichever is more frequent. A CCB must be run after the last CCV after the last sample.*	N/A	≤ 1 x MDL	within 3 x IDL for each analyte	< 3 x IDL for each analyte	≤ 1 x MDL	Evaluate instrument or system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Continue to perform system blanks until acceptance criteria are met. *Reanalyze the blank and associated investigative samples. If the absolute value of the blank exceeds the PQL, correct the problem, recalibrate instrument, verify the calibration, and reanalyze the preceding 10 analytical samples or all of the analytical samples analyzed since the last good calibration blank.*	All samples following the last acceptable CCB must be reanalyzed.	If the average recoveries are not within 3 standard deviations of the background mean, terminate analysis, correct the problem, recalibrate the instrument. Re-analyze the previous 10 investigative samples.	Cause of the problem must be determined, corrected, and all samples analyzed since the last acceptable CCB must be re-analyzed. If a lab consistently has concentration values > 3 x IDL, the IDL may be indicative of an estimated IDL, and must be re-evaluated	All samples following the last acceptable CCB must be reanalyzed.
Equipment Blank	5% of all decontaminations performed on each type of equipment	target analytes <1 x MDL; 5-10 x MDL for laboratory-induced contaminants	See GR	See GR	See GR	See GR	Suggests that field sampling-induced contamination may have occurred. Evaluate all associated QC samples. If all other QC samples are within prescribed acceptance limits, but the equipment blank is not (e.g., positive identifications of target analytes are observed), *contact the USEPA immediately to determine whether resampling and/or reanalysis is required.*	See GR	See GR	See GR	See GR
Method Blank (MB)	5% or 1 per batch (whichever is more frequent)	Absolute value < PQL	< 1 x MDL; or 10% of lowest concentration for each analyte.	< 1 x MDL except for common laboratory contaminants which may be 5-10 x MDL. *If any analyte concentration is > PQL, the lowest conc. of that analyte in the associated samples must be 10x more than the conc. found in the blank*	< 1 x MDL except for common laboratory contaminants which may be 5-10 x MDL. *If any analyte concentration is > PQL, the lowest conc. of that analyte in the associated samples must be 10x more than the conc. found in the blank*	< 1 x MDL; or 10% of lowest concentration for each analyte.	Evaluate instrument, locate source of contamination, perform system blanks to confirm that the system blank meets performance criteria. Re-analyze method blank and associated samples. *If method blank is still above the acceptance criteria, re-extract or redigest the method blank and all associated samples.*	See GR	See GR	See GR	See GR

Table 3.7.2: QC Requirements and Recommended Corrective Action for Metals

QC Performed	Minimum Frequency	Acceptance Criteria					Recommended Corrective Action				
		General Requirements (GR) *	GFAA Method 7060 & 7421	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A	General Requirements (GR)	GFAA Method 7000	ICP Method 6010 B	ICP/MS Method 6020	CVAA Method 7471A
Instrument Blank (IB)	5% or 1 per batch (whichever is more frequent)	N/A	N/A	N/A	N/A	N/A	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meet acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	N/A	N/A	N/A	N/A
System Blank	as required, if other blank samples are not meeting acceptance criteria	< 1 x MDL	See GR	See GR	See GR	See GR	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meet acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	See GR	See GR	See GR	See GR

* General Requirements should be followed in all cases, except where the requirements of the method are specified. In those cases, follow general requirements as stated and then refer to specific requirements for each method.

Method Detection Limit
lative Percent Difference
actical Quantitation Limit
strument Detection Limit
andard Reference Material
A - Not Applicable

Table 3.7.3: QC Requirements and Recommended Corrective Action for Anions

QC Performed	Minimum Frequency	Acceptance Criteria		Recommended Corrective Action	
		General Requirements (GR) [a]	Ion Chromotography Method 9056	General Requirements (GR)	Ion Chromotography Method 9056
Field Duplicate (FD) / Field Splits	If field duplicates have been collected for any of the samples identified for evaluation, they will be submitted. In the event that field duplicates are not available, up to 3 split samples will be prepared for each analysis.	RPD < 25% or,the absolute difference should not exceed 1 x MDL. A graphical comparison of the original and field duplicate samples should also be prepared. Recoveries will also be monitored using control charting. Control charting will be performed in accord with standard USEPA protocols and will be used to establish site specific performance criteria. This comparison will include a linear regression and will report the calculated correlation coefficient. R should be >0.9.	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples are factors in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-prep the method duplicate and associated investigative samples.*	See GR
Blind Standard	10% of all surface soil samples.	Accuracy requirements will be provided by the certifying laboratory. Recoveries will also be monitored using control charting. Control charting will be performed in accord with standard USEPA protocols and will be used to establish site specific performance criteria.	See GR	Verify the percent recovery calculations. If calculations are correct, the RPM will request the analyst to reanalyze the sample. If reanalysis results are still outside of acceptance limits, submit another blind standard immediately into the sample stream to determine if the analysis shows a trend or an isolated event. *Analysis of site samples may be discontinued until the problem is resolved.*	See GR
Blind Field Split (BS)/ Blind Field Duplicate	5% of all surface soil samples. (1 field duplicate per 20)	RPD < 25% or,the absolute difference should not exceed 1 x MDL. A graphical comparison of the original and field duplicate samples should also be prepared. Recoveries will also be monitored using control charting. This comparison will include a linear regression and will report the calculated correlation coefficient. R should be >0.9. Additionally, control charting will be performed in accord with standard USEPA protocols and will be used to establish site-specific performance criteria.	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples are factors in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-prep the method duplicate and associated investigative samples.*	See GR

Table 3.7.3: QC Requirements and Recommended Corrective Action for Anions

QC Performed	Minimum Frequency	Acceptance Criteria		Recommended Corrective Action	
		General Requirements (GR) [a]	Ion Chromotography Method 9056	General Requirements (GR)	Ion Chromotography Method 9056
Matrix Spike (MS)	5% or 1 per batch (whichever is more frequent)	N/A	75-125% recovery of known value	Verify the matrix spike percent recovery calculations and evaluate the LCS percent recoveries. If the calculations are correct and the LCS recoveries are acceptable, determine if matrix interference is a factor in the poor recoveries. If matrix effects are not observed, re-prep the matrix spike and associated investigative samples. *If appropriate, re-prep and reanalyze the matrix spike and associated investigative samples.*	Interference test must be conducted (see SW-846 Method 9056 for description of interference tests).
Laboratory Control Sample (LCS)	1 per 10 samples	must be within manufacturer's established acceptance limits.	See GR	Verify the percent recovery calculations. Evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the LCS and associated investigative samples. If necessary, recalibrate the instrument. *Do not continue analysis until the problem is solved.*	Re-run the LCS one time, if still not acceptable, all samples analyzed after the last acceptable LCS must be re-prepped and re-analyzed.
Method Duplicate (MD)	5% or 1 per batch (whichever is more frequent)	RPD < 25% (if 5 x MDL), or the absolute difference <1 x MDL	See GR	Verify the RPD calculation. If this is correct, determine if matrix interference or heterogeneous samples is a factor in the poor RPD. If matrix effects or heterogeneous samples are not observed, reanalyze the method duplicate and associated investigative samples. *If appropriate, re-prep and reanalyze the method duplicate and associated investigative samples.*	See GR

Table 3.7.3: QC Requirements and Recommended Corrective Action for Anions

QC Performed	Minimum Frequency	Acceptance Criteria		Recommended Corrective Action	
		General Requirements (GR) [a]	Ion Chromotography Method 9056	General Requirements (GR)	Ion Chromotography Method 9056
Initial Calibration Verification (ICV)	Beginning of each run *and end, after the last analytical sample;* or beginning of every new shift (whichever is more frequent)(after the ICB)	Prepare separate calibration curves for each anion of interest using a minimum of 3 concentration levels. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an acurate calibration curve to be established. Calibration standards should be based on expected concentrations, or defined by the working range of the detector.	90-110% recovery of known value.	Verify the percent recovery calculations. If calculations are correct, evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the ICV. If the results are still outside of the acceptance range, an entirely new calibration curve must be prepared for that analyte. *Do not continue analysis until the problem is solved.*	Calibration curves must cover the appropriate concentration range. That is, be at or below the PQL.
Initial Calibration Blank (ICB)	Beginning of each run or beginning of every new shift (whichever is more frequent)(before the ICV)	N/A	< 3 x PQL for each analyte.	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meets acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	Determine the cause, correct the problem, and recalibrate the instrument before any samples are analyzed.
Continuing Calibration Verification (CCV)	Every 10 samples in the analytical batch (after the CCB)	N/A	95-105% recovery of known value	Verify the percent recovery calculations. If calculations are correct, evaluate the standard to determine if it is faulty. If it is, prepare a new standard and reanalyze the CCV and all associated investigative samples. If necessary, recalibrate the instrument. *Do not continue analysis until the problem is solved. If std > control limits, stop analysis, correct problem, recalibrate instrument, verify calibration, and reanalyze all samples analyzed since the last good CCV.*	Discontinue sample analysis, determine cause of the problem, correct the problem, and recalibrate the instrument.

Table 3.7.3: QC Requirements and Recommended Corrective Action for Anions

QC Performed	Minimum Frequency	Acceptance Criteria		Recommended Corrective Action	
		General Requirements (GR) *	Ion Chromotography Method 9056	General Requirements (GR)	Ion Chromotography Method 9056
Continuing Calibration Blank (CCB)	every 10 samples in the analytical batch (before the CCV),*or once every 2 hrs. during the analytical run, whichever is more frequent. A* ***CCB must be run after the last CCV after the last sample.***	N/A	< 3 x PQL for each analyte.	Evaluate instrument or system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Continue to perform system blanks until acceptance criteria are met. *Reanalyze the blank and associated investigative samples. If the absolute value of the blank exceeds the PQL, correct the problem, recalibrate instrument, verify the calibration, and reanalyze the preceding 10 analytical samples or all of the analytical samples analyzed since the last good calibration blank.*	All samples following the last acceptable CCB must be reanalyzed.
Equipment Blank	5% of all decontaminations performed on each type of equipment	target analytes <1 x MDL; 5-10 x MDL for laboratory-induced contaminants	See GR	Suggests that field sampling-induced contamination may have occurred. Evaluate all associated QC samples. If all other QC samples are within prescribed acceptance limits, but the equipment blank is not (e.g., positive identifications of target analytes are observed), *contact the USEPA immediately to determine whether resampling and/or reanalysis is required.*	See GR
Method Blank (MB)	5% or 1 per batch (whichever is more frequent)	< 1 x MDL except for common laboratory contaminants which may be 5-10 x MDL *If any analyte concentration is > PQL, the lowest conc. of that analyte in the associated samples must be 10x more than the conc. found in the blank.*	See GR	Evaluate instrument, locate source of contamination, perform system blanks to confirm that the system blank meets performance criteria. Re-analyze method blank and associated samples. *If method blank is still above the acceptance criteria, re-prep the method blank and all associated samples.*	See GR
Instrument Blank (IB)	5% or 1 per batch (whichever is more frequent)	N/A	N/A	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meet acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	N/A

Table 3.7.3: QC Requirements and Recommended Corrective Action for Anions

QC Performed	Minimum Frequency	Acceptance Criteria		Recommended Corrective Action	
		General Requirements (GR) [a]	Ion Chromotography Method 9056	General Requirements (GR)	Ion Chromotography Method 9056
	as required; if other blank samples are not meeting acceptance criteria	< 1 x MDL	See GR	Evaluate system, locate source of contamination, and perform a system blank to determine if the system blank meets acceptance criteria. Perform instrument maintenance until analysis of system blanks meet acceptance criteria. *Do not begin analysis of investigative samples until criteria are met.*	See GR

[a] General Requirements should be followed in all cases, except where the requirements of the method are specified. In those cases, follow general requirements as stated and then refer to specific requirements for each method

MDL - Method Detection Limit
RPD - Relative Percent Difference
PQL - Practical Quantitation Limit
IDL - Instrument Detection Limit
N/A - Not Applicable

3.8 Data Validation and Useability

The following sections describe the requirements and methods for data review, validation and verification. In addition, the process for reconciling the data generated with the requirements of the data user is also defined.

3.8.1 Data Review Validation and Verification

The process of data review, validation and verification is intended to provide consistent and defensible analytical results. Analytical data generated as part of this project will be reviewed and verified before they are incorporated into the project database. Full data validation will be completed on approximately 5% of the data generated for this project. Abbreviated validation will be completed on 20% of the succeeding analytical data. Abbreviated and full data validation criteria are described in Section 3.8.2.

3.8.2 Validation

Full Validation: Full validation will be conducted on data packages for 5% of the samples submitted for chemical and physical analysis. This will be performed to ensure that data were produced in accord with procedures outlined in this project plan. The following elements will be reviewed for compliance as part of the full data validation:

- Methodology
- Holding times
- Calibration
- Blanks
- Spikes
- Duplicates
- LCSs
- Practical Quantitation Limits
- Analyte identification
- Analyte quantitation

Abbreviated Validation/Verification: Abbreviated validation will be completed on 20% of the analytical results for which full validation was not performed. This will be performed to ensure that data were produced in accord with procedures outlined in this

project plan. The following elements will be reviewed for compliance as part of the abbreviated data validation:

- Methodology
- Holding times
- Calibration
- Blanks
- LCSs
- Spikes
- Duplicates

3.8.3 Final Reporting

Data reporting consists of communicating summarized data in a final form. QA for reporting consists of measures intended to avoid or detect human error and to correct identified errors. Such methods include specification of standard reporting formats and contents of measures to reduce data transcription errors.

Laboratory Reports: All raw data and analytical results will be provided by the commercial laboratory. This information will be incorporated into a final report. Copies of the raw analytical data packages will be submitted to USEPA for archival.

Study Report: A draft report of all the summary study design characteristics, sample analyses, data quality, correlation results and resulting field and analytical data shall be presented by the prime contractor. Simple (descriptive) statistical tests for the treatment group treatment will be performed and presented. Other statistical tests, as discussed in Section 2.0, will also be presented. This report will undergo technical review by USEPA. If necessary, comments to the draft report will be provided to the prime contractor and a final report will be issued.

3.9 Reconciliation with Data Quality Objectives

Information obtained from the VBI70 Pilot-Scale Soil Characterization Study will be evaluated through the data quality assessment (DQA) process to determine if the data obtained are of the correct quality and quantity to support their intended use. The DQA process consists of five steps as summarized below (USEPA 1996, 1998d).

Review the DQOs and Sampling Design: DQO outputs will be reviewed to ensure that they are still applicable. The sampling analysis and data collection documentation will also be reviewed for completeness and consistency with DQOs.

Conduct a Preliminary Data Review: Data validation reports will be reviewed to identify any limitations associated with the analytical data. Basic statistics will be utilized where applicable and meaningful graphs of the data will prepared as described in Section 3.8. This information will be used to learn about the structure of the data and to identify patterns, relationships or potential anomalies/outliers.

Select the Statistical Test: The most appropriate statistical procedure for summarizing and analyzing the data will be selected based on the review of the DQOs, the sampling design and the preliminary data review. Key underlying assumptions will be identified that must hold true for the statistical procedures to be valid.

Verify the Assumptions of the Statistical Test: The statistical test will be evaluated to determine whether the underlying assumption holds or whether departures from the assumptions are acceptable given the actual data or other information about the study.

Draw Conclusions from the Data: Calculations required for the statistical test will be completed and inferences drawn as a result of these calculations will be documented.

4.0 Data Management Plan

This Data Management Plan (DMP) describes a basic framework for the data management practices to be implemented during the performance of the VBI70 Pilot-Scale Soil Characterization Program. This section provides the details for obtaining, tracking, storing and managing data collected for the study. Data management applies to both hardcopy and electronic forms of data; therefore, procedures for both forms are addressed.

4.1 DMP Objectives

The objectives of this DMP are to:

- Describe the design of a database management system that is easily accessible for data retrieval, data evaluation, and data reporting.
- Outline the procedures that will be followed to assure that data collected during the investigation undergo proper QA/QC procedures and are organized in an appropriate database management system.
- Define responsibilities of individuals tasked with implementing the DMP.

4.2 General Data Configuration

This section describes the electronic data and hardcopy data that are anticipated to be generated during activities performed for this investigation. Data collection for this investigation will be centered primarily on the following data types:

- Laboratory Data – This will include results from the physical and chemical analyses performed on the soil/solid materials.

More details of the data collection procedures can be found in the Study Design (Section 2.0) of this project plan. Data will be maintained in both electronic and hard copy forms. For the electronic database, each data type (physical characteristics, metals concentrations, speciation, etc.) will be stored in an individual table within the database. A relationship between the tables will be established, so that the tables may be merged and queried as needed. Hardcopy data may be generated for numerous activities within this investigation. Examples of hardcopy data include chain-of-custody forms, instrument printouts from analytical laboratories, etc. This DMP discusses the procedures that will be used to store hardcopy data.

In addition to filing the hard copy forms in the project files, information from hard copy forms will be entered into the project database when appropriate. This DMP includes a discussion of the QA/QC procedures that will be used to assure that data are entered correctly and accurately.

4.3 Electronic Data Management

Data generated during this investigation will be managed using a database management system that provides an effective framework to handle the diversity and volume of anticipated data. In addition to meeting the needs of data users, the database management system will incorporate the following capabilities:

- Store tabular data (such as analytical results, qualifier codes, criteria used for qualitative decisions) in a relational database management system.
- Allow the user to query multidisciplinary data and readily integrate those data for decision-making.
- Allow assignment of unique identifiers for data.
- Provide an audit trail for sample tracking, including a QA program to minimize erroneous data entry.
- Allow integration of new data.
- Document the database structure, code definitions, and means of accessing information.
- Report tabular data.

The following sections present descriptions of how the database management system will store, access, and secure project electronic data.

4.3.1 Data Storage Structure

A database consists of conceptual and physical design components. The conceptual design integrates the intended function, contents, and products of the project database; the procedures for data entry and electronic data incorporation; the needs of data users; and compatibility requirements (within database software limitations). The physical design implements the conceptual design through programming, data incorporation, and built-in software functions.

Electronic data in tabulated format will be stored and retrieved through a Microsoft Access® database. The main components of Access® databases are tables, relationships between tables, and queries. Tables store the data in a structure consisting of rows and columns. Relationships define how data in one table relate to data in another table. Queries store the framework for selecting subsets of data from tables. The following sections discuss the anticipated structure for storing data for each of the expected types of data.

Laboratory Data

- Sample ID#
- Parameter Measurement (pH, metals concentration, etc.)
- Qualifier
- Units
- Collection Date
- Analysis Date
- Laboratory Name
- Laboratory Batch or Job #

4.4 Hardcopy Data Management

Many documents will be gathered, transferred, and generated during this investigation. The term "document" refers to any relevant information in hardcopy form (e.g., reports, raw and validated analytical data, figures, etc.). Documents gathered or generated in support of this investigation will be stored in a central project file. When documents are received, they will be filed in the project files. Document file categories include Bulk Soil Characterization Data, Stable Lead Isotope Ratios, Metals Concentration Data, Speciation Data, and In Vitro Bioaccessibility Data. Additional categories, such as criteria used for qualitative decisions may be added as necessary. If documents are transferred from one party to another, letters of transmittal will accompany external document transfers and will be retained on file as records of document transfer.

A checkout system will be used for hardcopy and electronic documents in project files. Whenever feasible, checked-out information will be returned and re-filed the same day. When this is not feasible, checked-out information will be subject to the same security protection as filed data. At the end of the project, the project file will be checked to ensure that all checked-out material has been returned.

4.5 Data Transfer

During sample analysis at the laboratory, analytical results will be either entered into the laboratory information management system or directly downloaded from the analytical instrument. The data will be reviewed in the laboratory for errors or omissions to assure that the data are reported in the correct format. Upon completion of these efforts, the laboratory will submit electronic data deliverables and hard-copy raw data to the Data Manager or other parties as specified by the laboratory subcontract. Where possible, the laboratory will provide an electronic data deliverable which has been formatted to the appropriate structure. If this is not possible, the electronic data will be translated by the Data Manager into the format necessary for inclusion in the project database, checked for incorrect information, and loaded into the database management system. The Data Manager will notify the appropriate project staff of any inconsistencies, omissions, or errors with the electronic data deliverables that require correction. These parties will work with the appropriate laboratory personnel to correct any problems.

Data which are received in hard-copy format only will be entered manually by the data management staff. All data transfer activities will follow appropriate QA/QC procedures as detailed in the following section.

4.6 Quality Assurance/Quality Control

When data are manually entered by the data management staff, they will be entered and compared to the hard copies to identify discrepancies and allow for their correction. One hundred percent of data which are manually entered will be verified against the hard copy reports. When data are electronically transferred, a portion of the electronic data (20%) will be verified against the hard copy reports.

Standard data reports and queries that are prepared will be tested by the Data Manager to assure that the data in the report matches the information contained in the database. Other tests may include comparisons of counts of certain data against expected totals.

4.7 Data Security

Protection of important data from damage, loss, corruption, or vandalism is a critical component of data management. Database security will be implemented and maintained throughout the project. Access to the full database will be restricted to personnel designated by the Project Coordinator. For example, authorized database users will be able to read or query the databases, but only designated personnel will be able to add to or change the database contents. The database will be backed-up daily or more often when active data entry/incorporation is taking place. During other times, the database will be backed-up following any changes.

4.8 Implementation of Data Management Plan

Responsibilities for implementing this DMP are described below. It should be noted that these responsibilities can be held by a single person or delegated to other individuals as appropriate. However, it is the responsibility of the person identified to ensure that tasks are completed. The responsibilities for each task are summarized below.

Project Coordinator – The Project Coordinator retains the final responsibility for all aspects of the project and project team. The Project Coordinator will support communications with subcontractors. The Project Coordinator is ultimately responsible for the individual project files as part of the work efforts completed to address the requirements of this investigation.

Data Manager – The Data Manager has the primary responsibility for maintaining the project databases and evaluating the data that will be included in the project database. This position reports directly to the Project Coordinator.

Specifically, the Data Manager is responsible for the following:

- Providing technical support to the Project Coordinator and Task Managers;
- Coordinating, setting priorities, and providing technical direction in implementing and maintaining the project data;
- Ensuring that analytical and/or field data are properly entered and the appropriate QA/QC steps have been taken;
- Controlling access to electronic data;
- Authorizing database changes and access;
- Coordinating data management audits;
- Ensuring that the requirements of the DMP are met;
- Defining and implementing database design;
- Assisting the project team with data queries;
- Performing database QA tests;
- Processing electronic laboratory data into the project database; and
- Reviewing data entry and resolving discrepancies.

Laboratory Project Manager – Although the analytical laboratory is a subcontracted service, the cooperation of laboratory personnel is essential to successful data management. Coordination of laboratory efforts and tasks completed under this subcontract will be addressed by the Laboratory Project Manager. The Laboratory Project Manager is ultimately responsible for the accuracy and completeness of laboratory deliverables. The Laboratory Project Manager is also responsible for the performance of the data validation effort to evaluate the quality of the laboratory analytical data in accordance with the requirements set forth in the QAPP (Section 3.0). This position reports directly to the Project Coordinator and works closely with the Task Managers and the Data Manager. The Laboratory Project Managers duties relating to data management include the following:

- Responsible for tracking sample analytical status;
- Responsible for maintaining communication between the laboratory and the project team and coordination of the transfer of laboratory reports and analytical results;
- Receiving and reviewing all chemical analytical data;
- Ensuring that chain-of-custody (COC) records are properly completed and maintained;
- Communicating with the Project Coordinator and laboratory regarding incomplete laboratory deliverables, analytical errors, data omissions, or data inconsistencies;
- Performance of validation of the laboratory results in accordance with the QAPP; and
- Approving release of validated chemical analytical data to the Data Manager for inclusion into the database.

5.0 References

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USEPA. 1999a. Draft Report for the Vasquez Boulevard and I-70 Site Residential Risk-Based Sampling Stage I Investigation. Prepared by ISSI Consulting Group, Inc. April 1999.

USEPA. 1999b. Project Plan for the Vasquez Boulevard and I-70 Site Phase III Field Investigation. Prepared by ISSI Consulting Group, Inc. August 4, 1999.

APPENDIX A: STANDARD OPERATING PROCEDURES

ON-FACILITY FIELD SAMPLING SOPS

A.1 Surface Soil Sampling for Metals

A.2 Test Pit Sampling at Smelter Facilities

TECHNICAL STANDARD OPERATING PROCEDURE

SURFACE SOIL SAMPLING FOR METALS

Date: September 1, 1999 (Rev. # 0) SOP No. ISSI-VBI70-07

Title: SURFACE SOIL SAMPLING FOR METALS

APPROVALS:

Author: _____ ISSI Consulting Group, Inc. Date: _____

SYNOPSIS: A standardized method for sampling surface soils for metals determination is described. Protocols for sample collection, sieving, compositing, and sample handling are provided.

Received by QA Unit:

REVIEWS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
EPA Region VIII	Bonita Lawton / RPM	9/10/99
ISSI Consulting Group, Inc.	WS Bratton	9/13/99

SURFACE SOIL SAMPLING PROCEDURES

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a standardized method for surface soil sampling to be used by employees of EPA Region VIII, and contractors/subcontractors supporting EPA Region VIII projects and tasks. This SOP describes the equipment and operations that should be used for sampling surface soils, in order to provide reproducible data. Site-specific deviations from the procedures outlined in this document must be approved by the EPA Region VIII Regional Project Manager, Regional Toxicologist, or On-Scene Coordinator prior to initiation of the sampling activity.

This SOP provides protocols for two different types of surface soil sampling methods: discrete sampling and composite sampling. Depending on the data quality objectives outlined in the Project Plan, one of the following methods is appropriate.

2.0 RESPONSIBILITIES

Successful execution of the Project Plan requires a clear hierarchy of assigned roles with different sets of responsibilities associated with each role.

The Project Leader may be an EPA employee or contractor who is responsible for overseeing the surface soil sampling activities. The Project Leader is also responsible for checking all work performed and verifying that the work satisfies the specific tasks outlined by this SOP and the Project Plan. It is the responsibility of the Project Leader to communicate with the Field Personnel specific collection objectives and anticipate situations that require any deviation from the Project Plan. It is also the responsibility of the Project Leader to communicate the need for any deviations from the Project Plan with the appropriate EPA Region VIII personnel (Regional Project Manager, Regional Toxicologist, or On-Scene Coordinator).

Field personnel performing soil sampling are responsible for adhering to the applicable tasks outlined in this procedure while collecting samples at residences. The field personnel should have limited discretion with regard to collection procedures, but should exercise judgment regarding the exact location of the Sample Point, within the boundaries outlined by the Project Leader.

3.0 EQUIPMENT

- Soil coring tool - Various makes of coring tools are acceptable and selection of the specific brand and make of tool should be at the discretion of the contractor performing the sampling. Selection of the coring tool should be based on the individual characteristics of the soil to be sampled (e.g. clay, stony, soft etc.). At a minimum, the tool should be capable of retrieving a cylindrical plug of soil of the dimensions specified in the Project Plan. A soil coring tool of this type is typically fabricated from stainless steel, has a hollow stem, is T-shaped and uses two handles to apply the force necessary for core collection. A plunger is used to press out the soil plug from the tip of the coring device. Plungers may be fitted with an adjustable stop to allow all but a given length of soil to be pushed from the coring tool. In all cases the procedures recommended by the manufacturers should be followed with regard to use of the coring tool. Coring tools with disposable plastic sleeves may be employed to minimize the decontamination effort.

- Collection containers - type to be specified in the Project Plan. Containers may be glass jars, plastic jars, or plastic bags.

- Scoop/spoon - for collecting surface soil samples. May be plastic or stainless steel. Must be lead free and unpainted.

- Gloves - for personal protection and to prevent cross-contamination of samples. May be plastic or latex. Disposable, powderless.

- Field clothing and Personal Protective Equipment - as specified in the Project Plan.

- Squeeze bottle -for dispensing potable (drinking) quality water. Used to clean and decontaminate sampling equipment. Bottles should be labeled "Drinking Water".

- Squeeze bottle - for dispensing deionized water. Used to clean and decontaminate sampling equipment. Bottles should be labeled "DI Water".

- Wipes - disposable, paper. Used to clean and decontaminate sampling equipment.

- Field notebook -used to record progress of sampling effort and record any problems and field observations.

- Permanent marking pen - used to label sample containers.

- Sieves - if specified in the Project Plan. U.S. Standard # 10 (capable of passing material < 2 mm) and U.S. Standard # 60 (capable of passing material < 250 μm). Used to remove gravel and debris in the field to minimize shipping weight. Sieves mesh should be constructed of stainless steel or plastic and designed for soil processing.

- Measuring tape or pocket ruler -used to measure the length of soil core in the soil coring device.

- Plastic Buckets - used to receive rinse water generated in the course of sampling and sieving equipment cleaning.

- Trash Bag - used to dispose gloves and wipes.

- Laboratory Surfactant – used for equipment decontamination. Alconox is a brand in common use.

4.0 SAMPLING PATTERN

Discrete sampling requires soil collection from a single location and is used as a measure of the concentration at a single Sample Point. Composite sampling requires soil collection from multiple (sub-sample) points. These soils are then mixed and used as a measure of the concentration averaged over the entire area (zone).

The Project Plan will specify the pattern and order of sample collection. If compositing is to be done, the Project Plan will identify the areas and patterns used to group samples.

Care should be taken to avoid tracking soil from one area to another. As samples are taken sequentially, care should also be taken not to contaminate an area yet to be sampled with the residue of the sample that is currently being taken. In general, one should move in a single direction through the sampling area. If an area is known or suspected of having a higher concentration of metals, all other considerations being equal, it should be sampled last to prevent cross contamination.

5.0 COLLECTION OF DISCRETE SURFACE SAMPLES USING A SOIL CORING DEVICE

A new pair of plastic gloves are to be worn at each Sample Point.

Locate the Sample Point on the ground specified by the Project Plan and clean the area free of twigs, leaves, and other vegetative material that can be easily be removed by hand. If the specified Sample Point is occupied by a rock, cobble or other hard objects of sufficient size that are incapable of easy removal by hand, move the Sample Point to the closest accessible location.

Place the soil coring tool on the ground and position it vertically. Holding the tool handle with both hands, apply pressure sufficient to drive the tool to a depth specified in the Project Plan, while applying a twisting force to the coring tool. Remove the tool by pulling up on the handle while simultaneously applying a twisting force. If the sample was retrieved successfully, a plug of soil approximately two inches long should have been removed with the coring tool.

If the Project Plan calls for coring of soil covered by turf-like vegetation (lawn), the coring tool should be pushed through the sod and the root mass extracted along with the soil core.

Hold the soil coring tool horizontally or place it on the ground. Place the coring tool plunger with the two inch stop inside the coring tool and push the soil plug out of the coring tool until the stop is encountered and two inches of soil remains inside. Using a clean spatula or knife, remove the soil collected at depth greater than the required length from the end of the sampling tool. Remove the stoppered plunger from the soil coring tool and using the unstoppered plunger, push the two-inch soil plug from the coring tool so that it falls directly into the sample container. If the auger is not equipped with a plunger, use a scoop or spoon to push the soil plug into the collection container. Seal, label, and store the container as specified in the Project Plan.

Decontaminate the equipment as described in Section 12.0.

6.0 COLLECTION OF DISCRETE SOIL SAMPLES USING A SCOOP

A new pair of plastic gloves are to be worn at each Sample Point.

Locate the Sample Point on the ground specified by the Project Plan and clean the area free of twigs, leaves, and other vegetative material that can be easily be removed by hand.

If the specified Sample Point is occupied by a rock, cobble or other hard object of sufficient size to be incapable of easy removal by hand, move the Sample Point to a the closest accessible location.

Open a clean sample container. Using the metal spoon or scoop, excavate a hole in the soil with the sampling dimensions specified in the Project Plan, while placing the excavated material directly inside the sample container. The sides of the excavated hole should be close to vertical to avoid sampling that is biased in favor of the upper layer of soil. Seal, label, and store the container as specified in the Project Plan.

Decontaminate the equipment as described in Section 12.0.

7.0 COLLECTION OF COMPOSITE SAMPLES USING A CORING TOOL

A new pair of plastic gloves are to be worn in each Sampling Zone.

Follow the procedures described in Section 5.0, repeating the procedure until all of the sub-samples from a given zone have been collected in the sample container. The number of sub-samples included in each composite will be specified in the Project Plan. After all of the sub-samples have been collected, seal, label, and store the container as specified in the Project Plan.

Decontaminate equipment as described in Section 12.0.

8.0 COLLECTION OF COMPOSITE SAMPLES USING A SPOON OR SCOOP

A new pair of plastic gloves are to be worn in each Sampling Zone.

Follow the procedures described in Section 6.0, repeating the procedure until all of the sub-samples from a given zone have been collected in the sample container. The number of sub-samples included in each composite will be specified in the Project Plan. After all of the sub-samples have been collected, seal, label, and store the container as specified in the Project Plan.

Decontaminate equipment as described in Section 12.0.

9.0 SITE CLEAN-UP

The Project Plan will address the methods used to fill holes generated by the sampling procedure. In general, it is desirable to fill sampling holes with clean, moist topsoil. The material should be poured into the hole and tamped down lightly.

Rinse water, the roots of vegetation removed during sampling, and any unused soil generated in the course of sieving must be disposed of as specified in the Project Plan. This material should be handled and disposed in accordance with state and federal regulations.

10.0 RECORDING KEEPING AND QUALITY CONTROL

A field notebook should be maintained by each individual or team that is collecting samples, as described in the Project Plan. The Project Plan will detail specific conditions which require attention, but at a minimum the following information should be collected.

This notebook information must include:

- date
- time
- personnel
- weather conditions
- a sketch of the sampling pattern that is filled in with sample identification numbers as the samples are collected
- locations of any samples and sub-samples that could not be acquired
- descriptions of any deviations to the Project Plan and the reason for the deviation.

Samples taken from soils with visible staining or other indications of non-homogeneous conditions should be noted. Draw a diagram that details the residence of each yard. Sample locations and sample numbers should be identified on the diagram. Field personnel will collect the proper type and quantity of quality control samples as prescribed in the Project Plan.

11.0 SAMPLE PREPARATION

Because humans are thought to be more likely to ingest and inhale fine soil particles than coarse soil particles, sieving is usually required to obtain particle sizes that will provide

data suitable for human health risk assessment. The Project Plan will include details on particle size requirements.

The option of whether to sieve soils prior to shipment to the laboratory as well as the location of sieving operations should be specified in the Project Plan. Soil sample must be dried and sieved in a controlled environment rather than in the field.

11.1 Drying the Soils

If the sample is a composite, the sub-samples should be mixed prior to drying. Soils must be sufficiently dry prior to sieving. This may be determined by performing a "squeeze" test. The soil plug is pinched between a freshly gloved thumb and index finger. If the soil fragments and becomes powdery, the sample may be regarded as adequately dry for sieving. Alternatively, if soil squeezed in the palm of a freshly gloved hand becomes cohesive and retains its shape after squeezing, the soil has too much moisture for sieving.

If samples are not sufficiently dry, they should be air-dried by being allowed to stand in an open or partially covered sample container for 24 hours. Air-drying should be carried out in a warm room with moderate air circulation. If the soil is still too moist, it should be left to air dry for another 24 hours and tested again.

Rough guidelines for soil drying times are as follows:

- Sandy soil (24 hours)
- Silty soil (24 - 48 hours)
- Clayey soil (36 - 60 hours)

If samples are still not dry after these periods of air-drying or if drying times must be expedited, oven-drying may be necessary. Oven-dried samples will be dried to constant weight at 100 °C.

Once soil samples have been determined to be adequately dry, the sample plug or scoop should be manually crushed and broken up by squeezing the material with a freshly gloved hand. If the sample contains a section of grass sod, the soil should be shaken from the grass roots allowing this soil to mix with the other soil that will be sieved. The grass sod plug should be subjected to the screening process along with the other soil. Under no circumstances should the sample be ground (either against itself or against the compositing bowl or the sieving screens) as grinding generates particles that would not otherwise exist as part of the soil matrix.

11.2 Sieving

Sieving will be performed for each sample using clean equipment. Unprocessed soils (defined here as "raw soil") should first be sieved using a #10 screen, allowing particles <2 mm to pass through its mesh. Soils passing through a #10 screen will be defined here as "bulk soil". The bulk soil should then be sieved using a #60 screen, allowing particles <250 μm to pass through its mesh. Soils passing through a #60 screen are referred here as fine soil ("fines"). The screens may be stacked with the #10 screen on top and the #60 screen below. Covers (top and bottom) may be used as part of the sieving process if they are designed as part of the sieve set.

Sieving should be performed by pouring the soil sample on top of the sieve and shaking the screen rapidly back and fourth so that the material rolls over the screen mesh. The screen should occasionally be tapped against a hard surface to allow material to pass through mesh holes that have become clogged. Shaking should continue only as long as material above the screen contains particles smaller than the mesh opening. The screening process should not be used to break-up fragments of the soil core and materials should not be rubbed against the screen as a way of making them pass through the mesh.

The screens should be thoroughly cleaned prior each use. Decontamination procedures are described in Section 10.0.

12.0 DECONTAMINATION

Because decontamination procedures are time consuming, having a quantity of sampling tools sufficient to support decontamination at a maximum of once per day is recommended. All sampling and sieving equipment must be decontaminated prior to reuse.

The procedures to decontaminate all equipment is outlined below:

1) Remove visible soil.
2) Rinse equipment with potable water.
3) Rinse in a surfactant solution.
4) Rinse equipment with potable water.
5) Triple rinse with deionized water.

Washing should be performed by sequential immersion of the equipment in buckets partially filled with these solutions. If necessary, a brush should be used to remove soil

material from screens and coring tools. Equipment should be set on clean toweling to dry. Equipment should be visibly dry before being used again.

Wipes, gloves, and rinse solutions must be disposed or stored properly as specified in the Project Plan.

13.0 GLOSSARY

Project Plan - The written document that spells out the detailed site-specific procedures to be followed by the Project Leader and the Field Personnel.

Sample Point - The actual location at which the sample is taken. The dimensions of a sample Point are 3/4" in diameter and 2" deep (core technique) or 2" across by 2" deep (spoon/scoop technique).

Discrete Sampling - A sample program in which material taken from a single Sample Point.

Composite Sampling - A sample program in which multiple Sample Points are compiled together and submitted for analysis as a single sample.

Sample zone - A unit of surface area subjected to a given sample program. A given zone usually is thought to contain similar metals concentrations or to be defined by a single set of exposure parameters.

Raw soils - Soil with sticks, leaves and debris removed but otherwise unprocessed.

Bulk soils - Raw soil that has passed through a U.S. Standard #10 sieve (< 2 mm).

Fine soil - Bulk soil that has passed through a U.S. Standard #60 sieve (< 250μm).

14.0 REFERENCES

USEPA, 1995. Residential Sampling for Lead: Protocols for Dust and Soil Sampling, Final Report, EPA 747-R-95-001, USEPA, March 1995, 38 p.

American Society for Testing and Materials, 1995. Standard Practice for Field Collection of Soil Samples for Lead Determination by Atomic Spectrometery Techniques, ASTM Designation: E 1727 - 95, October 1995, 3 p.

Attachment 1
SOIL DATA SHEET

PHASE: SC

MEDIUM: Yard Soil

SAMPLE COLLECTION METHOD: ISSI-VBI70-07Revision 0

DEPTH: 0-2"

DATE: _____

SAMPLE TEAM ID: _____

SAMPLE LOCATION: _____
House Number Street Name

CLASS: FS (Field Sample)

SAMPLE NO.	SAMPLE TIME	SAMPLE TYPE *(circle one)*
		COMP GRAB
		COMP GRAB
		COMP GRAB
		COMP GRAB
		COMP GRAB

Date: September 1, 1999 (Rev. # 0) SOP No. ISSI-VBI70-08

Title: TEST PIT SOIL SAMPLING AT SMELTER FACILITIES

APPROVALS:

Author:_____ISSI Consulting Group, Inc. Date: _____

SYNOPSIS: A standardized method for collecting test pit soil samples at smelter facilities is described. Protocols for sample collection and handling are provided.

REVIEWS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
USEPA Region 8	Bonita Lavelle / RPM	9/10/99
ISSI Consulting Group, Inc.	WJ Bratton	9/13/99

1.0 PURPOSE

The purpose of this Standard Operating Procedure (SOP) is to provide a standardized method for test pit sampling at smelter facilities, to be used by employees of USEPA Region 8, or contractors and subcontractors supporting USEPA Region 8 projects and tasks. This SOP describes the equipment and operations used for sampling sub-surface soil at smelter facilities, to produce data that can be used to support risk evaluations. Deviations from the procedures outlined in this document must be approved by the USEPA Region 8 Remedial Project Manager or Regional Toxicologist prior to initiation of the sampling activity.

Collection and measurement of samples and the documentation of data will be performed as described in the associated procedures.

2.0 RESPONSIBILITIES

The Field Project Leader (FPL) may be an USEPA employee or contractor who is responsible for overseeing the field sampling activities. The FPL is also responsible for checking all work performed and verifying that the work satisfies the specific tasks outlined by this SOP and the Project Plan. It is the responsibility of the FPL to communicate with the Field Personnel regarding specific collection objectives and anticipated situations that require any deviation from the Project Plan. It is also the responsibility of the FPL to communicate the need for any deviations from the Project Plan with the appropriate USEPA Region 8 personnel (Remedial Project Manager or Regional Toxicologist).

Field personnel performing test pit soil sampling are responsible for adhering to the applicable tasks outlined in this procedure while collecting samples. The field personnel should have limited discretion with regard to collection procedures, but should exercise judgment regarding the exact location of the Sample Point, within the boundaries outlined by the FPL.

3.0 EQUIPMENT

- Stainless steel or plastic hand trowel – for collecting soil from the test pit walls.
- Collection containers - plastic zip-lock bags.
- Gloves - for personal protection and to prevent cross-contamination of samples. May be plastic or latex. Disposable, powderless.
- Field clothing and Personal Protective Equipment - as specified in the Health and Safety Plan.

- Field notebook -a bound book used to record the progress of the sampling effort and record any problems and field observations during sampling.

- Three-ring binder book- to store necessary forms used to record and track samples collected at the VBI70 site. Binders will contain the Surface Soil Data Sheet, Site Diagram, Test Pit Log, and sample labels for each day. Example forms are provided in Attachment 1 and Attachment 2.

- Permanent marking pen - used as needed during sampling and for documentation of field logbooks and data sheets.

- Squeeze bottle -for dispensing potable (drinking) quality water. Used to clean and decontaminate sampling equipment. Bottles must be labeled "drinking water".

- Squeeze bottle - for dispensing deionized water. Used to clean and decontaminate sampling equipment. Bottles must be labeled "DI".

- Trash Bag - used to dispose gloves and wipes.

- Laboratory Surfactant – used for equipment decontamination. Alconox is a brand in common use.

- Flagging Tape – used to mark sampling locations and/or distinct units on the wall of the test pit.

4.0 SAMPLING PROCEDURE

Before beginning the field test pit excavation program, office and field management personnel should obtain information about geologic conditions expected at the site. The investigation team should be composed of technical specialists with backgrounds in fields of geology, engineering geology, or geotechnical engineering. Mapping the trench walls and sampling should be conducted by the members of the investigative team. The construction subcontractor should be responsible for supplying excavation equipment, trained operators, materials for shoring the trench walls, and the preparation of the walls for mapping.

To the extent possible, test pits will be located at flue, baghouse, waste transfer or other historical facilities that may constitute a potential source of arsenic and lead. At each test pit location, samples will be collected from each distinct strata. If units are wider than 12

inches, samples will be collected at the following intervals: 0 to 1 feet, 1 to 2 feet, 2 to 3 feet, 3 to 4 feet, and 4 to 5 feet below the surface.

4.1 Trench Excavation

Excavate a trench with a backhoe that uses a 2- to 3-ft-wide bucket capable of efficient excavation to a depth of 5ft.

A. Remove and stockpile the topsoil before trench excavation. Make shallow cuts of 1- to 2-ft depth and stockpile the material on the downwind or downslope side of the trench. Maintain ample space (a minimum of 2 ft) between the stockpiled material and the trench to maneuver excavation equipment.

B. Maintenance of stable walls, particularly in deep trenches, is best accomplished with straight-line sections. Because shoring in corners or curve areas is potentially ineffective, avoid the excavation of nonlinear trenches.

C. Make trench walls vertical, uniform in width, and as smooth as practical to facilitate the efficient use of portable shoring braces. Safety precautions, including the use of shoring braces, trench access, and trench stability, are the responsibility of the contractor performing the excavation. At all times, relevant safety laws and precautions must be followed.

D. Place excavated subsoil as a windbreak on the upwind or upgradient side of the trench. Maintain sufficient space (a minimum of 2 ft) between the material and the trench edge to ensure that it will not fall back into the trench or impede the advancement of the backhoe.

E. Depending on the strength of the surficial deposits being trenched, mapping may occur concurrently with the advancement of the trench. The site geologist and an assistant should conduct the mapping of the trench wall at a safe distance behind the backhoe, lessening the risk of exposure to caving induced by backhoe vibrations. One team member should remain at the surface to direct the excavation activity and assist the trench wall mapping team. The topside member can ensure that the backhoe operator excavates the trench as specified by the site geologist, who should advise the backhoe operator of the trench conditions requiring immediate attention and direct the operator to trim and terrace walls when appropriate. The safety of the trench mappers is the paramount responsibility of the topside team member, who should be constantly alert for indications of potential wall caving (like tension

cracks). All persons entering any portion of the trench should wear personal equipment for protection of the head and eyes.

F. Plot physical attributes (see Attachment 2) of units that are distinct in terms of lithology, texture, or color, using feet and inches, plus or minus the baseline elevation and station position. In addition to bedding planes and lithologic interfaces, geologic features (like cobble strings) may aid in following stratum continuity, particularly if individual units are difficult to discern. Assessment of stratigraphy in a deposit lacking distinct strata or containing similar geologic units may be aided by the use of a 5-ft-square aluminum frame marked with string in a 1-ft grid pattern. Other features like large boulders of organic debris should also be mapped.

G. Visual Description. Description of the soil will be according to the ASTM Designation D 2488-84, Standard Recommended Practice for Description of soils (Visual-Manual Procedure).

H. The technical specialist assisting the mapper in the trench should prepare the trench wall ahead of the mapper using nails and string line and highlighted with plastic flagging tape. Physical support of the grid frame when mapping the middle and upper reaches of a trench wall will be the responsibility of this person.

I. At each sampling location, two photographs should be taken. The first should record the unaltered appearance of the wall. The second should record the same location after it has been divided into a grid reference using nails and string line and highlighted with spray paint. Take flash photos if ambient light is not sufficient for a clear, bright exposure.

J. Collect samples from the trench wall according to Section 4.2.

4.2 Soil Sample Collection

After each pit has been excavated with the backhoe, use a stainless steel or plastic trowel hand trowel to collect grab samples from each one-foot depth interval from the vertical wall of each pit. A minimum of 500 grams will be collected from each depth increment. The samples should be placed directly into the sample containers. Containers must be labeled according to the procedure described in Project Plan. The sample ID label, date, time of collection and a log of the sample will also be recorded in the field book, as described in Section 6.0. Seal, label, and store the container as specified in the Project Plan. Samples should be transported according to the procedures described in the Project Plan.

The backhoe bucket must be decontaminated between pits, using a portable steam pressure washer. The hand trowel must be decontaminated between each sample depth increment and location using the procedure described in Section 7.0.

5.0 SITE CLEANUP

It is important at most sites that the restored site is as close to the original surface contour as practical. Compact the backfill by wheel rolling with the backhoe or loader to accomplish this objective.

In pastureland or any place where restoration is required and vegetation cover is important, replace the topsoil that was excavated and stockpiled from the trench at the end of the restoration process. After the surface is wheel rolled and dressed down, restore the area as specified by the access agreement.

A. Fill the test pit to its original level.

B. Ensure that all equipment is accounted for, decontaminated and ready for transport.

C. Restore the site to presampling conditions.

D. Make sure the test pits are properly staked and the location ID is readily visible on the location stake.

6.0 RECORDING KEEPING AND QUALITY CONTROL

A field notebook should be maintained by each individual or team that is collecting samples, as described in the Project Plan. The Project Plan will detail specific conditions which require attention, but at a minimum the following information should be collected.

- date
- time
- personnel
- weather conditions
- a diagram of the sampling trench that is filled in with sample identification numbers as the samples are collected
- locations of any samples and sub-samples that could not be acquired
- descriptions of any deviations to the Project Plan and the reason for the deviation.
- photographs from each sample location

In addition, a test pit log must be completed for each trench. A sample logbook page and instructions for filling out the data form are included in Attachment 2. Field personnel will collect the proper type and quantity of quality control samples as prescribed in the Project Plan.

7.0 DECONTAMINATION

Because decontamination procedures are time consuming, having a quantity of sampling tools sufficient to support decontamination at a maximum of once per day is recommended. All sampling equipment must be decontaminated prior to reuse.

The procedure to decontaminate all hand-held sampling equipment is outlined below:

1) Remove visible soil.
2) Rinse equipment with potable water.
3) Rinse in a surfactant solution.
4) Rinse equipment with potable water.
5) Triple rinse with deionized water.

Washing should be performed by sequential immersion of the equipment in buckets partially filled with these solutions. If necessary, a brush should be used to remove soil material from screens and coring tools. Equipment should be set on clean toweling to dry. Equipment should be visibly dry before being used again.

Wipes, gloves, and rinse solutions must be disposed or stored properly as specified in the Project Plan.

8.0 REFERENCES

ASTM. 1986. Standard Recommended Practice for Description of Soils (Visual-Manual Procedure)," 411-25, ASTM D:2488-84. American Society of Testing Methods, Philadelphia, Pennsylvania.

HYDROMETRICS. 1995. Engineering Evaluation/Cost Analysis Workplan for Former Murray Smelter Site. Publication 339137-339138. September 1995.

ATTACHMENT 1

Logbook DCN _____

Attachment 1

SMELTER SOIL DATA SHEET

PHASE: SC

MEDIUM: Smelter Soil

SAMPLE COLLECTION METHOD: ISSI-VBI70-08 Revision 0

DEPTH: _____

DATE: _____

SAMPLE TEAM ID: _____

SAMPLE LOCATION: _____
Facility Code Location ID

CLASS: FS (Field Sample)

SAMPLE NO.	SAMPLE TIME	SAMPLE TYPE *(circle one)*
		COMP GRAB
		COMP GRAB
		COMP GRAB
		COMP GRAB
		COMP GRAB

ATTACHMENT 2

APPENDIX 5.2

TEST PIT LOG

TEST PIT LOG

PAGE 1 OF ____

FACILITY CODE ____ EXCAVATOR CODE ____

LOCATION ID ____ EXCAVATION DATE ____

COORDINATES (FT): DEPTH (FTFD) ____

NORTH ____ EAST ____ CONSTRUCTION METHOD ____

GROUND ELEVATION (FT MSL) ____ ACCEPTANCE CODE ____

LOCATION TYPE TP

GROUNDWATER LEVELS		
DATE	TIME	DEPTH (FT)

LOCATION DESCRIPTION

LITHOLOGIC LOG

LOGGER CODE ____

DEPTH (FT)	SAMPLE INTERVAL	SAMPLE METHOD	SAMPLE ID	USCS	VISUAL DESCRIPTION

ACCEPTANCE CODES: A–ACCEPTABLE R–RECONNAISSANCE U–UNACCEPTABLE N–NOT DETERMINED

CONSTRUCTION METHODS:

D – DUG
O – OTHER (SPECIFY)
T – TRENCHING

SAMPLE METHODS:

B – UNDISTURBED BLOCK
D – DISTURBED BULK

COMPLETE BOLDED DATA FOR ENTRY INTO TMS
TPD-004 (3/88)

FORM COMPLETED BY/DATE

TECHNICAL REVIEWER/DATE

TEST PIT LOG

PAGE ____ OF ____

FACILITY CODE _____

LOCATION ID _____ COMPLETION DATE _____

LITHOLOGIC LOG

DEPTH (FT)	SAMPLE INTERVAL	SAMPLE METHOD	SAMPLE ID	USCS	VISUAL DESCRIPTION

COMPLETE BOLDED DATA FOR ENTRY INTO TIMS
TPD-684 (3/88)

FORM COMPLETED BY/DATE

TECHNICAL REVIEWER/DATE

APPENDIX 5.3

DATA FORM COMPLETION INSTRUCTIONS

Use a pen with black ink that is not water soluble (not a felt-tip pen). Make an entry in each blank. Where there is no data entry, enter UNK for Unknown, NA for Not Applicable, or ND for Not Done. If any procedure was not performed as prescribed, give the reason for the change or omission on the form. To change an entry, draw a single line through it, add the correct information above it, and initial the change.

TEST PIT LOG

1. Facility Code. Five-character code abbreviating the facility name where program activity is being conducted. The first three characters indicate the facility, and the remaining two numbers designate the specific site within the facility.

2. Location ID. Four-character code assigned sequentially to each test pit location where physical, chemical, biological, radiological, and other measurements are taken.

3. Coordinates (Ft): North/East. The coordinates refer to the horizontal location of the test pit. At the time of the field investigation, the exact coordinate position of the borehole will not be known. In this case, UNK must be within the two spaces on the form. This information will be provided when the survey data comes in after the test pit program has been completed.

4. Ground Elevation (Ft MSL). At the time of the field investigation, the exact ground elevation of the test pit will not be known. In this case, the exact ground elevation will be determined when the survey data comes in after the program has been completed.

5. Location Type. This line is for data processing personnel only, and no additional information needs to be given on this line.

6. Excavator Code. Three-character code identifying the company responsible for excavating a test pit.

7. Excavation Date. The date when the test pit was excavated in the format DD-MMM-YY (01-JAN-88).

8. Depth (FTFD). The total depth of the test pit in feet and tenths of feet.

9. Construction Method. The construction or excavation method used in the advancement of the test pit. A table of various construction methods is included at the bottom of each Test Pit Log form.

10. Acceptance Code. One-character code assigned by the installation manager.

11. Groundwater Levels. The date, time, and depth (in feet) of any water encountered during the excavation of a test pit should be recorded by the distance from the ground surface to the location where it is seeping from the sides of the excavated trench.

12. Location Description. A written description of the approximate test pit location in respect to some nearby permanent topographic or geographic location.

13. Logger Code. Three-character code identifying the company that employs the person filling out the Test Pit Log form.

14. Lithologic Log

    a. Depth (Ft). A numerical designation that generally depicts lithologic soil boundaries. Each space is usually designated as equal to 1.0 ft of depth below the ground surface. Depths will be recorded on the Test Pit Log in feet and tenths of feet.

CONVERSION TABLE

(INCHES TO TENTHS OF FEET)

Inches	Tenths of Feet
1	.08
2	.17
3	.25
4	.33
5	.42
6	.50
7	.58
8	.67
9	.75
10	.83
11	.92
12	1.00

    b. Sample Interval. A graphical representation depicting the interval from which the sample was collected.

    c. Sample Method. The method by which the samples will be obtained. A list of test pit sampling methods is included at the bottom of each Test Pit Log form.

    d. Sample ID. Four-digit number assigned to ensure that data collected retains uniqueness from other data collected at the same location ID.

e. USCS (The Unified Soil Classification System). A method of grouping unconsolidated earth materials according to their engineering properties. It is based on soil behavior, which is a reflection of the physical properties of the soil and its constituents. The system established 15 distinct soil groups with different engineering properties. Boundary classifications are provided for soils having characteristics of 2 groups. The 15 soil groups are divided into the categories of fine-grained and coarse-grained materials and are described in Appendixes 5.4 and 5.5, respectively.

f. Visual Description. The visual description of material being excavated.

APPENDIX 5.4

CHECKLIST TO DESCRIBE FINE-GRAINED SOILS

1. Typical Name
   Sandy Silt, Silt, Clayey Silt, Sandy Clay, Silty Clay, Clay, Organic Silt, and Organic Clay

2. Size Distribution
   Approximate percent of gravel, sand, and fines in fractions finer than 3 inches

3. Color
   Note presence of mottling and banding, as well as color of the soil.

4. Moisture Content
   Dry, Moist, Wet, and Saturated

5. Consistency
   Soft, Firm (medium), Stiff, Very Stiff, or Hard

6. Structure
   Stratified, Laminated (Varved), Fissured, Blocky, Lensed, and Homogeneous (nonstratified)

7. Cementation
   Weak or Strong

8. Local or Geologic Name

9. Group Symbol

Soil Classification

Group Symbol	Group Name
CL	Lean clay (low plasticity)
ML	Silt
OL	Organic clay or silt (lean)
CH	Fat clay (high plasticity)
MH	Elastic silt
OH	Organic clay or silt (Fat)
PT	Peat

APPENDIX 5.5

CHECKLIST TO DESCRIBE COARSE-GRAINED SOILS

1. Typical Name
   Sand, Clayey Sand, Silty Sand, Gravel, Clayey Gravel, Silty Gravel, Cobbles, and Boulders

2. Gradation
   Well Graded (uniformly graded) or Poorly Graded (gap graded)

3. Size Distribution.
   Approximate percent of gravel, sand, and fines in fractions finer than 3 inches

4. Grain Shape
   Angular, Subangular, Subrounded, and Rounded

5. Color

6. Moisture Content
   Dry, Moist, Wet, and Saturated

7. Structure
   Stratified, Lensed, and Nonstratified

8. Cementation
   Weak and Strong

9. Local or Geologic Name

10. Group Symbol

Soil Classification

Group Symbol	Group Name
GW	Well-graded gravel
GP	Poorly graded gravel
GM	Silty gravel
GC	Clayey gravel
SW	Well-graded gravel
SP	Poorly graded gravel
SM	Silty sand
SC	Clayey sand

BULK SOIL CHARACTERISTICS SOPS

A.3 Particle-size Analysis

A.4 Minerology of Sands, Gravels and Clays

15 Particle-size Analysis[1]

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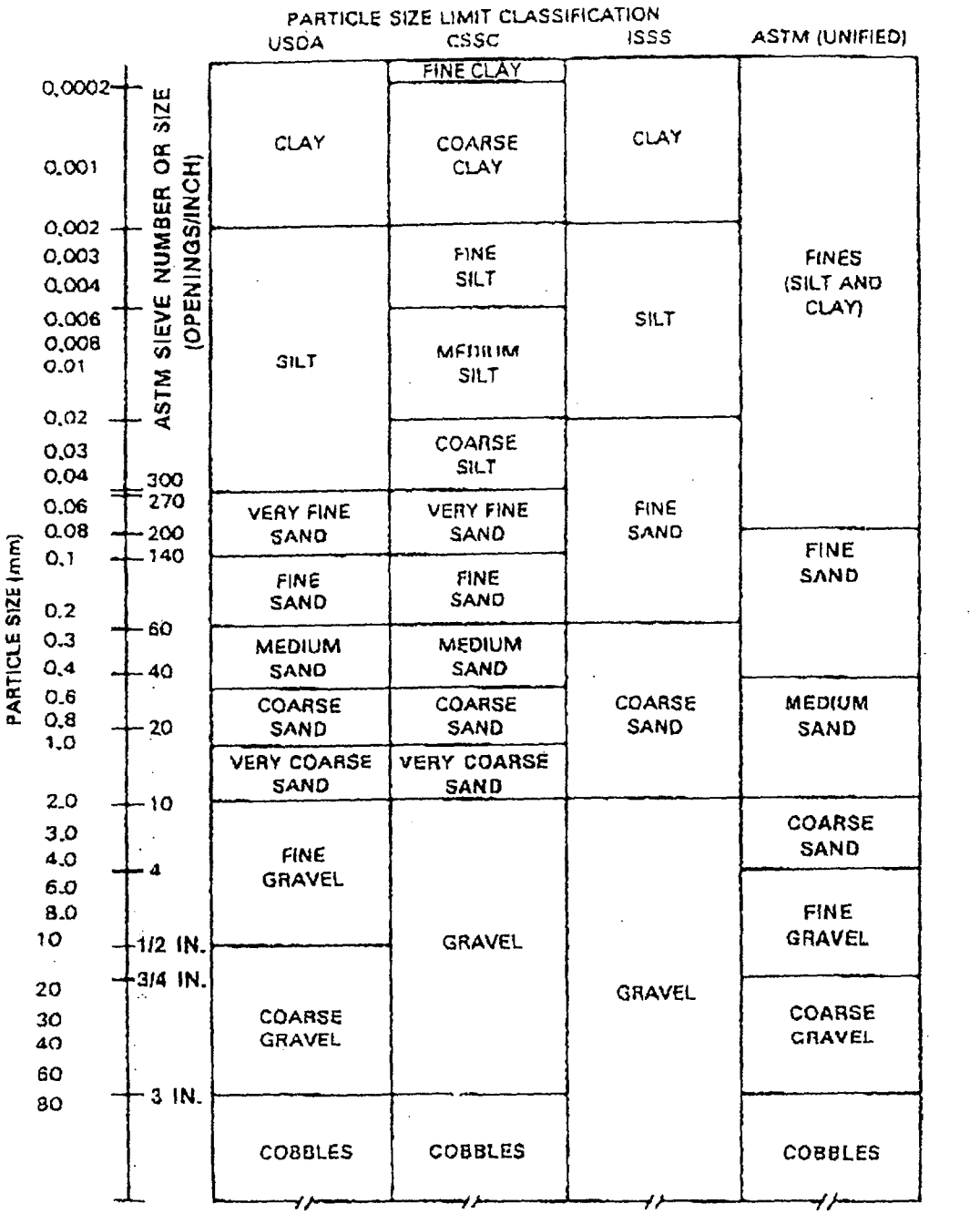
15-1 INTRODUCTION

Particle-size analysis (PSA) is a measurement of the size distribution of individual particles in a soil sample. The major features of PSA are the destruction or dispersion of soil aggregates into discrete units by chemical, mechanical, or ultrasonic means and the separation of particles according to size limits by sieving and sedimentation.

Soil particles cover an extreme size range, varying from stones and rocks (exceeding 0.25 m in size) down to submicron clays (< 1 μm). Various systems of size classification have been used to define arbitrary limits and ranges of soil particle size. Soil particles smaller than 2000 μm are generally divided into three major size groups: sands, silts and clays. These groups are sometimes called soil separates and can be subdivided into smaller size classes. Figure 15-1 shows the particle size, sieve dimension, and defined size class for the system of classification used by the U. S. Department of Agriculture (USDA), the Canadian Soil Survey Committee (CSSC), the International Soil Science Society (ISSS) and the American Society for Testing and Materials (ASTM). The American Society of Agronomy has adopted the USDA classification [i.e., sands ($<$2000–50 μm), silts ($<$50–2 μm), and clays ($<$2 μm)]. Although the USDA classification scheme will be emphasized in the following methods, it should be recognized that other systems are frequently cited, particularly in engineering literature, hence, care should be taken to specify clearly which system is being used when reporting results.

Particle-size analysis data can be presented and used in several ways, the most common being a particle-size distribution curve. An example of this type of curve is shown in Figure 15-2. The percentage of particles

[1]Prepared for the U.S. Department of Energy and the U.S. Nuclear Regulatory Commission under Contract DE-AC06-76RLO 1830.



USDA—U.S. DEPARTMENT OF AGRICULTURE, (SOIL SURVEY STAFF, 1975)
CSSC—CANADA SOIL SURVEY COMMITTEE, (McKEAGUE, 1978)
ISSS—INTERNATIONAL SOIL SCI. SOC. (YONG AND WARKENTIN, 1966)
ASTM (UNIFIED)—AMERICAN SOCIETY FOR TESTING & MATERIALS (ASTM, D-2487, 1985a)

Fig. 15–1. Particle-size limits according to several current classification schemes.

less than a given particle size is plotted against the logarithm of the "effective" particle diameter. Particle-size distribution curves, when differentiated graphically, produce frequency distribution curves for various particle sizes. Frequency curves usually exhibit a peak or peaks representing the most prevalent particle sizes.

Particle-size distribution curves are used extensively by geologists in geomorphological studies to evaluate sedimentation and alluvial pro-

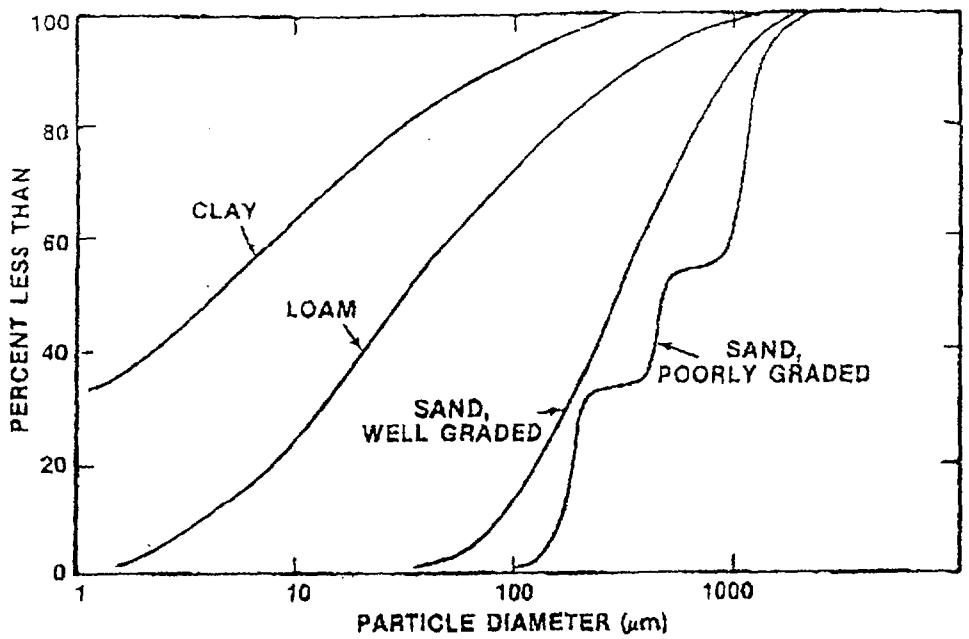


Fig. 15–2. Particle-size distribution curves for several soil materials (after Hillel, 1982).

cesses, and by civil engineers to evaluate materials used for foundations, road fills, and other construction purposes. Details of the use of these curves are given by Krumbein and Pettijohn (1938) and Irani and Callas (1963).

Particle-size analysis is often used in soil science to evaluate soil texture. Soils rarely consist entirely of one size range. Soil texture is based on different combinations of sand, silt, and clay separates that make up the particle-size distribution of a soil sample. Figure 15-3 shows the USDA defined limits for the basic soil textural classes. Details for interpretation of the textural triangle for soil classification purposes are given by the Soil Survey Staff (1975). The ASTM (Unified) engineering classification system is used widely for delineating soil types for construction purposes (Fig. 15-4). In this system, liquid limits and plasticity indexes must be known in order to properly classify the soil type (ASTM, 1985a,b).[2]

Hydrologists often use PSA as a means of predicting hydraulic properties, particularly for sands (Todd, 1964). Recently, Bloemen (1980) and Arya and Paris (1981) have used PSA as a means to predict water retention and unsaturated hydraulic conductivity of soils. These predictive methods appear to work best on sands or structureless soil materials.

15–2 PRINCIPLES

15–2.1 Pretreatment and Dispersion Techniques

Pretreatment of samples to enhance separation or dispersion of aggregates is a key step in PSA and is generally recommended, since many

[2] Stevens (1982) has published a BASIC program for computing the Unified (ASTM) classification for a tested soil. A BASIC program for computing the USDA textural classes is available upon request from the authors.

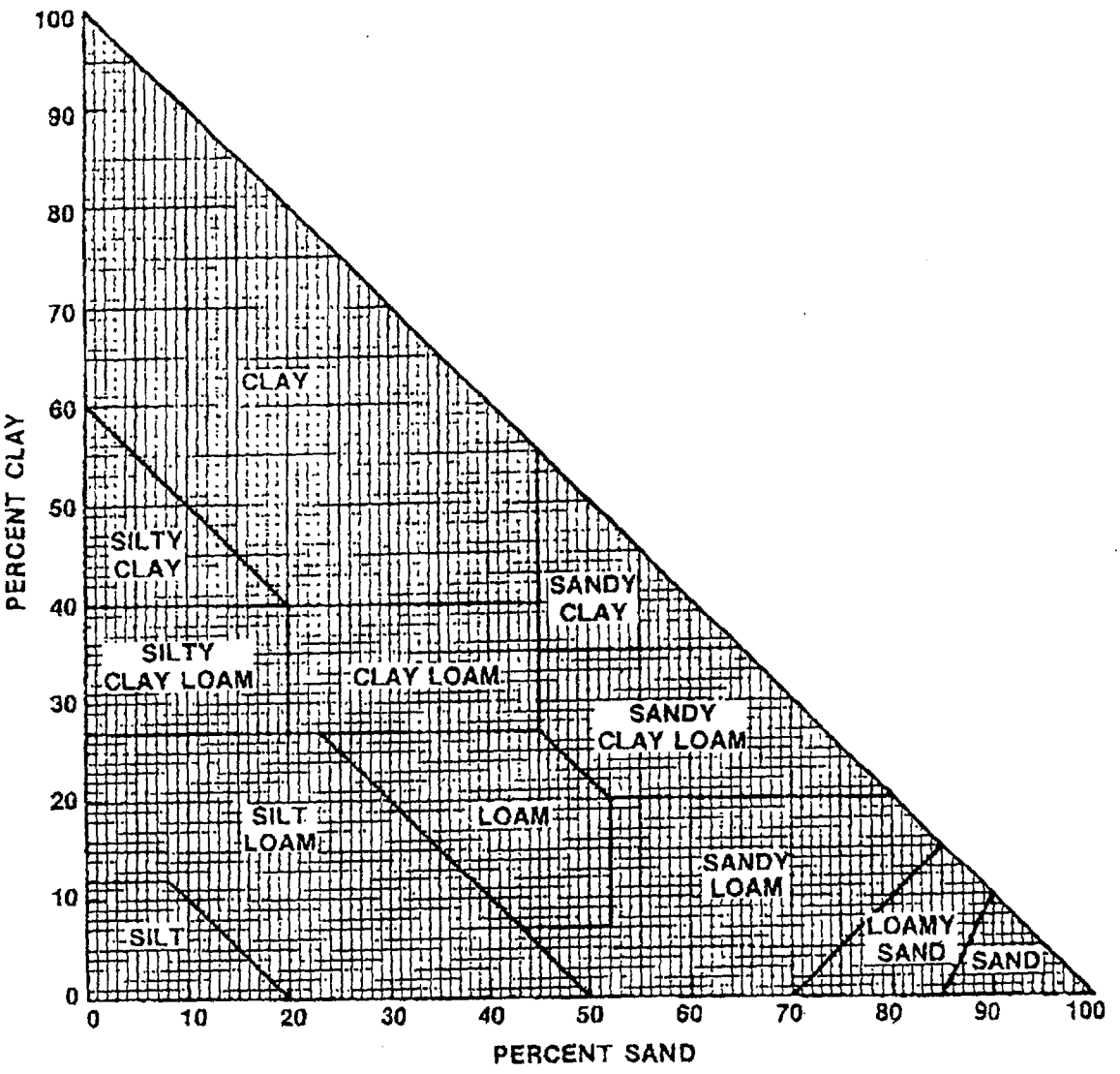


Fig. 15–3. Textural triangle for soil textural analysis using the USDA classification scheme.

soils contain aggregates that are not readily dispersed. Soils generally contain organic matter and often contain iron oxides and carbonate coatings that bind particles together. Chemical pretreatments are used for removal of these coatings; however, chemical treatment can result in destruction and dissolution of some soil minerals. Physical treatments are also used, but standardization of treatment and adequate testing of specific methods are needed, since the very process of separation by mechanical or ultrasonic means can fragment the individual particles into further subunits. Procedures should clearly specify the sample pretreatment, the separation method, and the purpose for which the size analysis is intended for a particular soil.

Standard PSA methods require that soil particles be dispersed in an aqueous solution by both chemical and physical means. After pretreatment, chemical dispersion is often accomplished using a dilute alkaline solution of sodium polyphosphate. The effectiveness of the chemical dispersing agent depends on its ability to create and maintain repulsive

forces between soil particles. Some soils (e.g., those of volcanic ash origin) that have been highly weathered disperse more readily in acid media; hence, some pretesting may be required to determine effects of soil mineralogy and other factors on soil dispersibility and to select an appropriate method to achieve complete dispersion. Physical dispersion of particles is accomplished by shearing action or turbulent mixing, using mechanical shakers, electrical mixers, or ultrasonic probes.

Dispersibility of soils low in organic matter depends primarily on soil mineralogy. Highly oxidized soils are particularly difficult to disperse. Examples include the "subplastic" soils of Australia (McIntyre, 1976; Brewer & Blackmore, 1976; Walker & Hutka, 1976; Blackmore, 1976; Norrish & Tiller, 1976). Depending on the method of chemical treatment and physical dispersion used, measured clay content for an individual soil sample can vary by factors of two to four or more.

Volcanic ash soils are high in amorphous (noncrystalline) clay-sized materials and have great resistance to dispersion, particularly after air or oven drying (Kubota, 1972; Schalscha et al., 1965; Espinoza et al., 1975; Maeda et al., 1977). Kubota (1972) reported clay contents ranging from 1 to 56 wt% for one volcanic ash soil, depending on pretreatment. Maximum clay content was obtained when the soil was retained at field moisture prior to ultrasonic dispersion. Warkentin and Maeda (1980) recommend that volcanic ash soils be left at field moisture and dispersed at either pH 3 or above pH 9. Tama and El-Swaify (1978) and El-Swaify (1980) have observed that soils with variable charge are particularly difficult to disperse unless the dispersant solution is well below or above the zero-point of charge.

Highly aggregated, stable clay soils may behave like coarse sands in terms of water infiltration; hence they may be identified in the field as sands or coarse loams. These same soils, having significant microporosity and high exchange capacities, retain water and nutrients much better than sands. For agricultural purposes, these soils should be texturally classed in a much finer category than they appear in the field. For soils where these uncertainties are known to exist, measurements such as a simple dispersive index (Sherard et al., 1976), ASTM dispersion test (ASTM, 1985c), or the water-stability of aggregates (see chapter 17) would be necessary and useful information. Also, a calculated clay content, determined from a ratio of the cation exchange capacity (CEC) of the total soil to the CEC of the clay-size material (Norrish & Tiller, 1976), can be used to estimate the theoretical maximum clay fraction of the soil material.

The method that produces the most complete dispersion of a soil sample is generally the more acceptable method. However, the chemical treatment and mechanical work done on the soil are dictated by somewhat arbitrary decisions, so there is no "absolute" size-distribution for a given sample. Intense mechanical or ultrasonic dispersion, coupled with appropriate chemical treatment, should yield a sample with most of the

Unified Soil Classification (ASTM—D2487)

Criteria for Assigning Group Symbols and Group Names Using Laboratory Tests[A]				Soil Classification: Group Symbol	Soil Classification: Group Name[B]
Coarse-Grained Soils More than 50% retained on No. 200 sieve	Gravels More than 50% of coarse fraction retained on No. 4 sieve	Clean Gravels Less than 5% fines[C]	Cu ≥ 4 and 1 ≤ Cc ≤ 3[E]	GW	Well-graded gravel[F]
			Cu < 4 and/or 1 > Cc > 3[E]	GP	Poorly graded gravel[F]
		Gravels with Fines More than 12% fines[C]	Fines classify as ML or MH	GM	Silty gravel[F,G,H]
			Fines classify as CL or CH	GC	Clayey gravel[F,G,H]
	Sands 50% or more of coarse fraction passes No. 4 sieve	Clean Sands Less than 5% fines[D]	Cu ≥ 6 and 1 ≤ Cc ≤ 3[E]	SW	Well-graded sand[I]
			Cu < 6 and/or 1 > Cc > 3[E]	SP	Poorly graded sand[I]
		Sands with Fines More than 12% fines[D]	Fines classify as ML or MH	SM	Silty sand[G,H,I]
			Fines classify as CL or CH	SC	Clayey sand[G,H,I]
Fine-Grained Soils 50% or more passes the No. 200 sieve	Silts and Clays Liquid limit less than 50	Inorganic	PI > 7 and plots on or above "A" line[J]	CL	Lean clay[K,L,M]
			PI < 4 or plots below "A" line[J]	ML	Silt[K,L,M]
		Organic	Liquid limit - oven dried / Liquid limit - not dried < 0.75	OL	Organic clay[K,L,M,N] / Organic silt[K,L,M,O]
	Silts and Clays Liquid limit 50 or more	Inorganic	PI plots on or above "A" line	CH	Fat clay[K,L,M]
			PI plots below "A" line	MH	Elastic silt[K,L,M]
		Organic	Liquid limit - oven dried / Liquid limit - not dried < 0.75	OH	Organic clay[K,L,M,P] / Organic silt[K,L,M,Q]
Highly organic soils		Primarily organic matter, dark in color, and orgnic odor		PT	Peat

Fig. 15–4. Unified soil classification system including plasticity chart (ASTM, 1985a). Continued on p. 389.

[A]Based on the material passing the 3-in. (75-mm) sieve.
[B]If field sample contained cobbles or boulders, or both, add "with cobbles or boulders, or both" to group name.
[C]Gravels with 5 to 12% fines require dual symbols:
GW-GM well-graded gravel with silt
GW-GC well-graded gravel with clay
GP-GM poorly graded gravel with silt
GP-GC poorly graded gravel with clay
[D]Sands with 5 to 12% fines require dual symbols:
SW-SM well-graded sand with silt
SW-SC well-graded sand with clay
SP-SM poorly graded sand with silt
SP-SC poorly graded sand with clay
[E]$Cu = D_{60}/D_{10}$ and $Cc = \frac{(D_{30})^2}{D_{10} \times D_{60}}$
[F]If soil contains ≥ 15% sand, add "with sand" to group name.
[G]If fines classify as CL-ML, use dual symbol GC-GM, or SC-SM.
[H]If fines are organic, add "with organic fines" to group name.
[I]If soil contains ≥ 15% gravel, add "with gravel" to group name.
[J]If Atterberg limits plot in hatched area, soil is a CL-ML, silty clay.
[K]If soil contains 15 to 29% plus No. 200, add "with sand" or "with gravel," whichever is predominant.
[L]If soil contains ≥ 30% plus No. 200, predominantly sand, add "sandy" to group name.
[M]If soil contains ≤ 30% plus No. 200, predominantly gravel, add "gravelly" to group name.
[N]PI ≥ 4 and plots on or above "A" line.
[O]PI < 4 or plots below "A" line.
[P]PI plots on or above "A" line.
[Q]PI plots below "A" line.

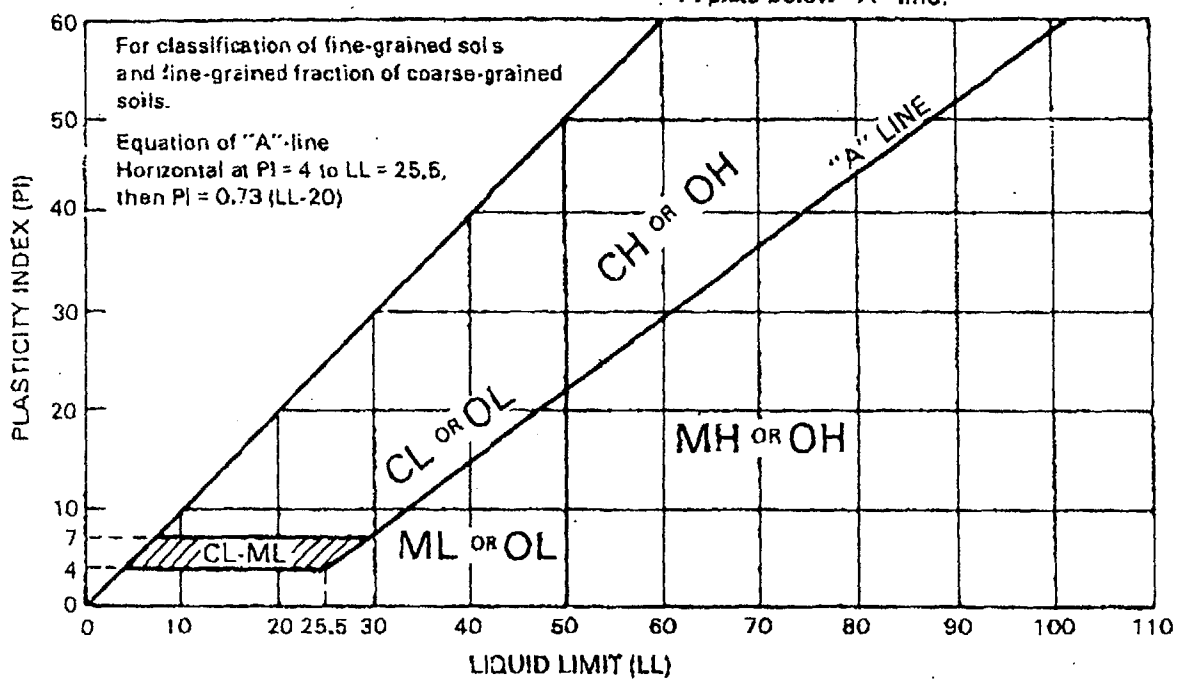


Fig. 15–4. Continued.

clay minerals in the measured clay fraction. In contrast, a less drastic chemical treatment and/or little mechanical dispersion may reflect the more "natural" particle-size distribution of the soil. Comparisons of PSA results should always include comparisons of the pretreatment and dispersion methods used.

15-2.1.1 ORGANIC MATTER REMOVAL

Removal of organic matter is often a first step in the chemical pretreatment of many soils. The necessity and difficulty of organic matter removal depends on the intended use of the analytical results of the PSA, the nature and concentration of organic matter in the sample to be analyzed, the pH of the soil, and the associated presence in the soil of free carbonates, gypsum, oxides, and soluble salts. A variety of reagents have been used in the past to successfully remove organic matter. Notable among these are hydrogen peroxide (H_2O_2), sodium hypochlorite, sodium hypobromite, and potassium permanganate. Hydrogen peroxide has been recommended as the standard oxidant for most soils (Day, 1965).

15-2.1.2 REMOVAL OF IRON OXIDE

Coatings and crystals of various iron oxides, such as hematite and goethite, often act as cementing and binding agents in soils. Removal of these cementing agents aids in dispersion of the silicate portion of the soil and is often necessary for accurate mineralogical analysis. Mehra and Jackson (1960) recommend the use of a bicarbonate-buffered, sodium dithionite–citrate system for iron oxide removal. This method, compared with several other methods for removal of free iron oxides from latosolic soils, was found to be the most effective. In addition, this method was the least destructive of iron silicate clays, as indicated by least loss of cation exchange capacity. Mehra and Jackson (1960) indicated that the optimum pH for maximum iron oxide removal was approximately 7.3. Since considerable OH^- is expended in the sodium dithionite–citrate reaction with iron oxide, a buffer is needed to hold the pH at the optimum level. Sodium bicarbonate has proven to be an effective buffer. This procedure minimizes the formation of sulfide, iron sulfide, zinc oxalate or other unwanted precipitates during iron oxide removal.

In soils where iron oxides are part of the dominant mineralogy, it is not recommended that iron oxides be removed, since many of the primary mineral grains in the clay fraction could be destroyed (El-Swaify, 1980).

15-2.1.3 REMOVAL OF CARBONATES

Removal of carbonate from soils prior to dispersion and sedimentation can be accomplished relatively easily by acidification of the sample. Heating accelerates the reaction. Samples that are acidified before organic matter removal with H_2O_2 will usually be free of carbonates. Hydrogen

chloride (HCl) treatment can cause destruction of crystalline lattice of clay minerals; therefore, acid treatment with 1 *M* NaOAC at pH 5 is preferred.

15-2.1.4 REMOVAL OF SOLUBLE SALTS

A variety of soluble salts including sodium, calcium, and magnesium chlorides and carbonates are commonly found in alkaline soils. High concentrations of soluble salts can cause flocculation of soil suspensions. Alkaline salts can cause decomposition of H_2O_2, decreasing its effectiveness as an oxidizing agent for soil organic matter. In addition, many soluble salts interfere with saturation of the exchange complex. Calcium and magnesium salts, commonly occurring as carbonates, are relatively unstable and are often measured as part of the clay and silt fractions.

The most common procedure for removal of soluble salts is to leach the salts with distilled water. Sample washing with distilled water can be accomplished by use of a filter candle or by centrifuging. The procedure should be repeated until the leachate salt concentration drops below 10 m*M*. The washing treatment is then followed by chemical and physical dispersion.

15-2.1.5 SAMPLE DISPERSION

Dispersion of soils is accomplished by a combination of methods. The methods for dispersion can be classified as either chemical or physical. Numerous methods of chemical dispersion have been investigated and reported (Theisen et al., 1968; Norrish & Tiller, 1976). Soils are chemically dispersed after oxidation of organic matter and removal of carbonates and iron oxides. Chemical dispersion is based primarily on the concept of particle repulsion, as a result of elevation of the particle zeta potential. This process is usually accomplished by saturating the exchange complex with sodium. Physical or mechanical methods of dispersion involve separation of the individual particles by means of some mechanical or physical process, such as rubbing, rolling, shaking, or vibrating. During the past 20 years, electronic dispersion, primarily by the use of ultrasonics, has become increasingly popular. Most researchers have found that a combination of chemical and physical or electronic methods provides the most complete and stable dispersion (Maeda et al., 1977; Mikhail & Briner, 1978).

15-2.1.5.1 Chemical Dispersion. Following removal of cementing and flocculating agents, samples must be dispersed and maintained in a dispersed state until sedimentation measurements are completed. A number of dispersing chemicals have been used. These include Na-hexametaphosphate (HMP), Na_2PO_7, NaOH, Na_2CO_3, and NaOBr. Of these, HMP appears to be the most commonly used dispersant. Commercial detergents contain quantities of HMP and other soluble phosphates, but uncertainty exists as to the exact amounts (Yaalon, 1976; Veneman, 1977).

For this reason, reagent grade HMP, which is commercially available, is the recommended chemical dispersant for the pipet and hydrometer tests described later in this chapter.

The exact amount of chemical dispersant needed to prevent flocculation is dependent on soil type (mineralogy, etc.). Flocculation often can be prevented by increasing the concentration of the dispersant solution. It should be noted that the pipet analysis requires only 0.5 g/L HMP, compared to a 5 g/L HMP solution for the hydrometer analysis. The lower amount needed for pipet analysis is likely due to pretreatment (organic matter, iron oxide, and soluble salt removal). Specific amounts used in these analyses have been established by empirical methods.

15–2.1.5.2 Physical Dispersion. Several methods of physical dispersion have been used in conjunction with pretreatment and chemical dispersion. The ASTM (1985d) recommends either an electric mixer with specially designed stirring paddles or an air-jet stirrer (Chu & Davidson, 1953; Theisen et al., 1968). For the hydrometer method, Day (1965) recommends a 5 min mixing with a standard electrical mixer (malted milk style), but cautions that the mixer blades deteriorate rapidly by abrasion and should be replaced after 1 or 2 h of use or when showing signs of wear. Reciprocating shakers have also been used. Overnight shaking is prescribed in the pipet procedure and can be used in the hydrometer method. However, the larger sample (40 g) used in the hydrometer method will pack to the bottom of 250 mL bottles; hence, larger (>500 mL) shaking bottles are recommended for the larger samples to avoid this problem. High-speed reciprocating shakers have been used effectively on small samples of 10 g or less (El-Swaify, 1980). These high-speed shakers optimize dispersion when the liquid-to-solid ratio is about 5:1.

15–2.1.5.3 Ultrasonic Dispersion. The principle behind ultrasonic dispersion is the transmission of vibrating sound waves in the soil solution. The sound waves produce microscopic bubbles, which collapse, producing *cavitation*. The release of intense energy of cavitation literally blasts the soil aggregates apart, causing dispersion even in highly aggregated soils.

Much work has been done in testing the use of ultrasonic dispersion of soils, but no standard procedures have been adopted (Edwards & Bremner, 1964, 1967; Saly, 1967; Bourget, 1968; Watson, 1971; Kubota, 1972; Mikhail & Briner, 1978). An initial concern with this method of dispersion was the possible destruction of primary particles, but Saly (1967) reported that ultrasonic vibration did not cause destruction of the crystalline lattice or breakdown of primary grains. Edwards and Bremner (1964, 1967) investigated the use of ultrasonic dispersion in the absence of a dispersing agent. For mineralogical analysis, ultrasonic dispersion was preferred, since dispersion was achieved without soil pretreatment or addition of a dispersing agent. Edwards and Bremner summarized the following advantages of ultrasonic dispersion: (i) the resultant suspension

is stable, hence flocculation does not occur during sedimentation; (ii) the method works well for dispersing calcareous soils, organic soils, and soils with high clay content; (iii) ultrasonic dispersion does not cause destruction of organic matter; and (iv) ultrasonic dispersion does not alter the soil pH, electrical conductivity, or cation exchange capacity. In contrast to the work of Edwards and Bremner, Mikhail and Briner (1978) reported that the most satisfactory method of pretreatment and dispersion involved the following steps; oxidation of organic matter, removal of carbonates and acid washing, and sodium saturation followed by ultrasonic dispersion. Their results indicated that the highest degree of dispersion was achieved by this technique. Kubota (1972) reported that a sonic dispersion at low pH was effective in dispersing peroxide-treated volcanic ash soils. Each of the above authors used a different ultrasonic power and dispersion time, indicating that effective dispersion with ultrasonics is soil dependent.

For routine PSA, there is no standard method for ultrasonic mixing proposed at this time. Much additional research is needed to determine the effectiveness or limitations of ultrasonic dispersion for a wide range of soil materials.

15–2.2 Sieving

The typical particle size range for sieving is 2000 to 50 μm. Several limitations of sieving have been noted in the past. Day (1965) indicated that the probability of a particle passing through a sieve in a given time of shaking depends on the nature of the particle, the number of particles of that size, and the properties of the sieve. Particle shape and sieve opening shape affect probability of passage. For example, a particle whose shape permits its passage only in one orientation has a limited chance of getting through, except after prolonged shaking. Sieve openings are generally unequal in size, and extensive shaking is required before all particles have had the opportunity of approaching the largest openings. In fact, it is rare that complete sorting of a given size range can be achieved. Good reproducibility requires careful standardization of procedure.

15–2.3 Sedimentation

Sedimentation analysis relies on the relationship that exists between settling velocity and particle diameter. Settling velocity is related to the diameter of a spherical particle in the following way. The force acting downward on each particle due to its weight in water is

$$F_{down} = 4/3\ \pi\ (X^3/8)\ (\rho_s - \rho_l)g \qquad [1]$$

where X = particle diameter, ρ_s = particle density, ρ_l = liquid density, and g = acceleration due to gravity. Because of the viscous resistance of the water, the opposing upward force is

$$F_{up} = 3 \pi X \eta v \quad [2]$$

where η = fluid viscosity and v = velocity of fall. The resisting force is zero where velocity, v, is zero at time $t = 0$, and it increases with increasing v until it is equal to the downward force. For sedimenting particles in a dilute dispersent solution, it can be shown that the terminal velocity for silt- and clay-size particles is reached in a relatively short time (a few seconds).

Equating F_{down} and F_{up} relates the terminal velocity to the particle diameter as follows:

$$v = g (\rho_s - \rho_l) X^2 / (18 \eta) . \quad [3]$$

A form of this relationship was first developed by Stokes (1851) and is now known as Stokes' Law. Basic assumptions used in applying Stokes' Law to sedimenting soil suspensions are:

1. Terminal velocity is attained as soon as settling begins.
2. Settling and resistance are entirely due to the viscosity of the fluid.
3. Particles are smooth and spherical.
4. There is no interaction between individual particles in the solution.

Gibbs et al. (1971) have shown that assumptions (1) and (2) are met by soil particles < 80 μm in diameter. Since soil particles are not smooth and spherical, X must be regarded as an "equivalent" rather than actual diameter. The assumptions of Stokes' Law as applied to soils are discussed fully by Krumbein and Pettijohn (1938).

In mineralogical analysis there is often a need to separate various clay fractions for specific analysis. The removal of the clay fraction by sedimentation can be accomplished by homogenizing a soil suspension and decanting all that remains above the plane $z = -h$ after time, t, where

$$t = 18 \eta h / [g (\rho_s - \rho_l) X^2] . \quad [4]$$

Quantitative separation by decantation requires that the residue be resuspended and decanted repeatedly to salvage those particles that were not previously at the top of the suspension at the start of the sedimentation period.

15-2.3.1 PRINCIPLE OF THE PIPET METHOD

The pipet method is a direct sampling procedure. It depends on taking a small subsample by a pipet at a depth h, at time t, in which all particles coarser than X have been eliminated. Using Stokes' Law in the form of Eq. [4], settling times for the clay fraction (<2 μm) can be calculated for sampling at a given depth for a given temperature. Table 15-1 lists sampling times for the clay fraction for a 10-cm sampling depth at selected temperatures for the pipet technique. Tables 15–2 and 15–3 list sampling

depths and times for various selected size fractions and specified settling times.

Experimental measurements with HMP solutions (Gee, unpublished data) show the following relationships for solution viscosity and density:

$$\rho_l = \rho^\circ(1 + 0.630\ C_s) \quad [5]$$

where

ρ_l = solution density at temperature t, g/mL,
ρ° = water density at temperature t, g/mL,
C_s = concentration of HMP, g/mL,

and

$$\eta = \eta^\circ(1 + 4.25\ C_s) \quad [6]$$

Table 15–1. Settling times for 2-μm clay at various temperatures. Calculated for a 10-cm sampling depth in distilled water, 0.5 g/L, and 5 g/L HMP solutions; with a particle density equal to 2.60 Mg/m³.

Temperature	Viscosity			Settling time		
	Distilled H_2O	0.5 g/L HMP	5.0 g/L HMP	Distilled H_2O	0.5 g/L HMP	5.0 g/L HMP
°C	10^{-3} kg m^{-1} s^{-1}			h		
18	1.0530	1.0553	1.0759	8.39	8.41	8.58
20	1.0020	1.0042	1.0238	7.99	8.00	8.16
22	0.9548	0.9569	0.9756	7.61	7.63	7.78
24	0.9111	0.9131	0.9310	7.26	7.28	7.42
26	0.8705	0.8724	0.8895	6.94	6.95	7.09
28	0.8327	0.8345	0.8508	6.64	6.65	6.78
30	0.7975	0.7992	0.8149	6.36	6.37	6.50

Table 15–2. Selected depths for 2-μm clay at specified times and temperatures, assuming a particle density of 2.60 Mg/m³ and dispersion with 0.5 g/L HMP solution.

Temperature	Viscosity	Sampling depth			
		4.5 h	5.0 h	5.5 h	6.0 h
°C	10^{-3} kg m^{-1} s^{-1}	cm			
20	1.0042	5.6	6.2	6.9	7.5
21	0.9800	5.8	6.4	7.0	7.7
22	0.9569	5.9	6.5	7.2	7.9
23	0.9345	6.0	6.7	7.4	8.1
24	0.9131	6.2	6.9	7.6	8.2
25	0.8923	6.3	7.0	7.7	8.4
26	0.8724	6.5	7.2	7.9	8.6
27	0.8532	6.6	7.4	8.1	8.8
28	0.8345	6.8	7.5	8.3	9.0
29	0.8166	6.9	7.7	8.4	9.2
30	0.7992	7.1	7.8	8.6	9.4

Table 15–3. Sampling times for 5-μm and 20-μm size fractions at a 10-cm sampling depth for pipet in 0.5 g/L HMP solution, over the temperature range 20 to 30°C for selected particle densities.

Temperature	5 μm Particle size			20 μm Particle size		
	Particle density (Mg/m³)			Particle density (Mg/m³)		
	2.4	2.6	2.8	2.4	2.6	2.8
°C	time (min)					
20	87.7	76.8	68.3	5.5	4.8	4.3
21	85.7	75.0	66.7	5.4	4.7	4.2
22	83.7	73.2	65.1	5.2	4.6	4.1
23	81.7	71.5	63.6	5.1	4.5	4.0
24	79.9	69.9	62.1	5.0	4.4	3.9
25	78.0	68.3	60.7	4.9	4.3	3.8
26	76.3	66.8	59.3	4.8	4.2	3.7
27	74.6	65.3	58.0	4.7	4.1	3.6
28	73.0	63.9	56.8	4.6	4.0	3.5
29	71.4	62.5	55.6	4.5	3.9	3.5
30	69.9	61.2	54.4	4.4	3.8	3.4

where

η = solution viscosity at temperature t, 10^{-3} kg m^{-1}s^{-1} (cpoise), and

η° = water viscosity at temperature t, 10^{-3} kg m^{-1}s^{-1} (cpoise).

Equations [5] and [6] apply to HMP solutions in the range of 0 to 50 g/L. For tests with HMP solution concentrations in the range 0 to 0.5 g/L, < 0.3% error in settling time results when the solution density is assumed to be that of pure water. Most settling-time calculations for pipet analysis (e.g., Day, 1965; Green, 1981) assume the dispersant solution has the viscosity of pure water. However, settling-time errors as great as 2% result from not correcting for increased viscosity when using 5 g/L HMP solutions. Water densities and viscosities at various temperatures are available from Weast (1983).[3]

Particle densities should be known with a precision of at least ± 0.05 Mg/m³. Settling-time errors in excess of 2% occur if particle densities are not known with at least this precision (see Table 15–3).

15–2.3.2 THEORY OF THE HYDROMETER METHOD

The hydrometer method, like the pipet method, depends fundamentally upon Stokes' Law, which for the hydrometer may be written as

$$X = 0t^{-1/2} \quad [7]$$

where 0 is the sedimentation parameter and is a function of the hydrometer settling depth, solution viscosity, and particle and solution density. This relationship follows from Eq. [4] by rearranging terms such that

$$X = (18\eta h'/[g(\rho_s - \rho_l)])^{1/2} t^{-1/2}. \quad [8]$$

[3]Note that Weast (1983) reports viscosity in centipoise (cpoise). For conversion to SI units, 1 cpoise = 10^{-3} kg m^{-1}s^{-1}.

Hence

$$\theta = (18\eta h'/[g(\rho_s - \rho_l)])^{1/2} \quad [9]$$

where h' = hydrometer settling depth, cm.

The hydrometer settling depth, h', is a measure of the effective depth of settlement for particles with diameter X. It can be related to the hydrometer stem reading, R, by considering the specific design and shape of the hydrometer (Kaddah, 1974; ASTM, 1983d). The relationship of the settling depth to the hydrometer dimensions can be approximated by

$$h' = L_1 + 1/2\,(L_2 - V_B/A) \quad [10]$$

where

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,
L_2 = overall length of the hydrometer bulb, cm,
V_B = volume of hydrometer bulb, cm^3, and
A = cross sectional area of the sedimentation cylinder, cm^2.

For the ASTM 152H hydrometer and a standard sedimentation cylinder: L_1 = 10.5 cm for a reading, R, of 0 g/L and 2.3 cm for a reading, R, of 50 g/L; L_2 = 14.0 cm; V_B = 67.0 cm^3; and A = 27.8 cm^2. Substitution of these values into Eq. [10] and solving in terms of R yields

$$h' = -0.164\,R + 16.3 \quad [11]$$

where R is the uncorrected hydrometer reading. The use of Eq. [11] and [8] to calculate particle diameter is detailed in section 15–5.2.5.

Sedimentation parameter values, θ, as a function of hydrometer readings, R, have been tabulated for the ASTM 152H hydrometer for temperatures of 30 °C by Day (1965) and for 20 to 25 °C by Green (1981). Correction factors for other temperatures and for particle densities other than 2.65 g/cm^3 are given by Day (1965). However, the use of Eq. [9] and [11] provides a straight-forward method to determine θ for any given temperature and particle density; hence tabulated θ values are not reported here.

ASTM 152H hydrometers are calibrated at 20 °C directly in terms of soil solution concentration, expressed as grams of soil per liter of solution (ASTM, 1985d). Correction of hydrometer readings for other temperatures and for solution viscosity and density effects is made by taking a hydrometer reading, R_l, in a blank (no soil) solution. This reading should be taken immediately after the uncorrected reading, R, is taken. The corrected concentration of soil in suspension at any given time is $C = R - R_l$, where C is expressed in g/L.

Differences in particle density for different soils affect particle settlement time, hence requires the correction of hydrometer readings and sedimentation parameter values. However, Gee and Bauder (1979) and

ASTM (1985d) show that moderate changes in particle density have only small effects on a given size determination. For example, errors in particle density of ± 0.1 g/cm^3 result in errors of $< \pm 0.5$ wt% clay for soils with clay contents up to 50 wt%.

15-3 SAMPLE PREPARATION

15-3.1 Apparatus

1. Drying trays
2. Wooden rolling pin
3. Sodium hexametaphosphate (HMP) solution (50 g/L)
4. Sieves. Large 20.5 cm (8 in.) diameter, with a 2 mm (2000 μm) square hole screen.
   Other screen sizes needed include: 5, 20, and 75 mm (USDA 1982); 5 mm (#4), 13 mm (1/2 in.), 20 mm (3/4 in.), 25 mm (1 in.), 50 mm (2 in.), and 75 mm (3 in.) (ASTM, 1985d).
5. Ruler or caliper capable of measuring to 250 mm (10 in.).

15-3.2 Method

Spread the bulk sample thinly (in 2 to 3 cm thick layers, maximum) on trays and air-dry. Thoroughly mix and roll the sample with a wooden rolling pin to break up clods to pass a 2-mm sieve. Sieve out the >2-mm size fractions. Continue rolling and sieving until only coarse fragments that do not slake in water or HMP solution remain on the 2-mm screen. Use a rubber roller for samples with easily crushed coarse fragments. Sieve larger size fractions, record weights, and use total sample weight to calculate the percentage of total sample < 2 mm.

15-3.3 Comments

Sometimes it is desirable to keep the sample at field moist conditions. If this is determined appropriate, force the field moist sample through the 2-mm screen by hand, using a large rubber stopper, double bag the sample in plastic, and store for further use. From a separate subsample determine the water content, so that a check can be made on possible drying effects during storage.

Whether material over 2 mm in diameter is sieved depends on the purpose for the data set. For soil survey purposes, methods specified by the USDA (1982) may be used. For engineering purposes, the material >2 mm can be sieved according to requirements specified by ASTM method D-2487 (ASTM, 1985a).

Sample size depends upon the maximum size fragments present. Suggested sample sizes are:

1. Particles up to 20 mm diameter -use 5 kg or more

2. Particles up to 75 mm diameter—use 20 kg or more
3. Particles up to 250 mm diameter—use 100 kg or more.

Because of the large samples required, the volume percent of particles coarser than about 20 mm is usually estimated. A suggested procedure for handling coarser fragments follows.

Weigh and sieve the entire sample through 75- and 20-mm screens. Weigh the >75-mm and the 75- to 20-mm fractions. Take a subsample of the <20-mm fraction for laboratory processing. Weigh the <20-mm sample before and after air-drying and correct the total sample weight for the loss of water from field conditions. Separate and weigh the 2- to 5-mm and the 5- to 20-mm fractions. If fine earth adheres to the coarse fraction, wash the coarse material, dry, reweigh, and apply the appropriate corrections. Calculate the coarse fractions as a percentage of the <20 mm material (or the <75 mm or the <250 mm depending upon the size limit involved in sampling). Note that for taxonomic (classification) purpose, stones or rock fragments >250 mm (10 in.) are separated and used to estimate the volume of coarse fragments for family placement of soils. A large caliper or ruler can be used to check the dimensions of the >250-mm material. In addition, weight measurements and volume displacement techniques can be used to evaluate coarse fragment volume.

15–4 PIPET METHOD

The pipet method is often used as a standard method from which other PSA methods are compared. This procedure has been adapted from Day (1965) and Green (1981).

15–4.1 Apparatus and Reagents

1. Beakers—100 mL to 1000 mL; centrifuge bottles, both glass and plastic—250 mL.
2. Centrifuges—low speed, about 1500 rpm, and high speed, about 12 000 rpm, with 250-mL bottles.
3. Filter candle—Porus ceramic tube, 0.05 MPa (0.5 bar) pressure rated.
4. Shakers—horizontal reciprocating shaker, sieve shaker, wrist action shaker, holders for 250-mL centrifuge bottles on paint shaker.
5. Cylinders—1000 mL (height of 1000-mL mark, 36 ± 2 cm).
6. Large (no. 13) rubber stoppers for 1000-mL cylinder.
7. Stirrers—electric stirrers for mechanical mixing (available from Soil Test, Inc., Evanston, IL, or other source),[4] hand stirrer made by joining a brass rod about 50 cm long to the center of a thin circular piece of perforated brass or plastic sheeting. The circular plate should

[4]Trade names are used in this chapter solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee of the product, nor does it imply an endorsement over other products not mentioned.

be cut to fit easily into the sedimentation cylinder. A 6-cm-diameter plate is normally adequate. If brass is used, place a wide rubber band around the edge of the brass sheeting to prevent scratching of the cylinder.

8. pH meter.
9. Pipet rack—device to permit sliding the pipet laterally and lowering the pipet to a percise depth in the sedimentation cylinder (Clark, 1962; Day, 1965; see also Fig. 15–4).
10. Lowy pipets—25 mL capacity (available from Sargent-Welch Co., Skokie, IL, or similar source).
11. Weighing bottles—(beakers can be used).
12. Set of sieves—square mesh with bronze wire cloth, 7.6 cm (3 in.) diameter with the following openings: 1000, 500, 250, 106, 53, or 47 μm.
13. Reagents—hydrogen peroxide (~30%); 1 *M* NaOAc (adjusted to pH 5); citrate–bicarbonate buffer: prepare 0.3 *M* sodium citrate (88.4 g/L) and add 125 mL of 1 *M* sodium bicarbonate (84 g/L) to each liter of citrate solution; sodium dithionite (hydrosulphite); saturated NaCl solution; 10% NaCl solution; 1 *M* $AgNO_3$; 1 *M* $BaCl_2$; acetone; Na-hexametaphosphate (HMP), 50 g/L stock solution; 1 *M* $CaCl_2$; 1 *M* HCl.

15–4.2 Procedures

15–4.2.1 PRETREATMENT

15–4.2.1.1 Removal of Carbonates and Soluble Salts. Weigh a small portion of the <2-mm fraction of air-dry soil into a 250 mL centrifuge bottle (10 g for clays, 20 g for loams, 40 g for sandy loams and loamy sands, and 80 g for sands). Weights are optional, but these are generally suitable if clay samples are required for mineralogy. Add approximately 100 mL of water, mix, and add 10 mL 1 *M* NaOAc (adjusted to pH 5). Centrifuge (about 10 min at 1500 rpm) until the supernatant is clear, then pour it off. Wash the soil twice by shaking with 50 mL of water, centrifuging and discarding the centrifugate if it is clear. If the centrifugate is not clear (as is often the case for soils containing high amounts of soluble salts and soils containing gypsum), further washing may be necessary. Washing through a filter candle to remove salts is a permissible substitute for centrifugation, but this procedure takes considerably longer than centrifugation. Check for salts by testing with $AgNO_3$ for Cl^- and $BaCl_2$ for SO_4^{2-}.

15–4.2.1.2 Removal of Organic Matter. After carbonate removal, add 25 mL of water to the soil in the centrifuge bottle, and shake on a wrist action shaker. Transfer samples containing high amounts of organic matter (>5%) to 1000 mL beakers. Add 5 mL of (H_2O_2) to the soil suspension, stir, cover, and observe closely for several minutes. If ex-

cessive frothing occurs, cool the container in cold water. Add more H_2O_2 when the reaction subsides. Note that MnO_2 decomposes H_2O_2, so if present in measurable amounts, steps should be taken to complex or remove before peroxide treatment. Heat to 90 °C when frothing has ceased, remove cover, and evaporate excess water (do not take to dryness). Continue peroxide and heat treatment until most of the organic matter has been destroyed (as judged by the rate of reaction and the bleached color of the sample). Rinse down the sides of the reaction vessel occasionally. Heat for about an hour after the final addition of peroxide to destroy excess peroxide. Transfer the sample to a 250-mL glass centrifuge bottle.

15–4.2.1.3 Removal of Iron Oxides. Add citrate-bicarbonate buffer to the peroxide treated sample in the centrifuge bottle to bring the total volume of solution to approximately 150 mL. Shake to disperse the soil. Add 3 g of sodium dithionite ($Na_2S_2O_4$) gradually, as the sample may froth. Put the bottle into a water bath at 80° C and stir the suspension intermittently for 20 min. Remove the sample from the bath, add 10 mL of saturated NaCl, mix, centrifuge, and decant off the centrifugate. It may be combined with subsequent centrifugates, if any, and analyzed for dithionite-extractable Fe, Al, Mn, etc. If the sample is completely gray (gleyed), proceed to the next step. If brownish color remains, repeat the previous step. Wash the sample once with 50 mL of citrate–bicarbonate buffer plus 20 mL of saturated NaCl (shake, centrifuge, and decant). Wash the sample twice with 50 mL of 10% NaCl, then twice with 50 mL of distilled water. If the wash solution is not clear, transfer the sample to a plastic centrifuge bottle and centrifuge at high speed. If this fails to yield clear centrifugate, add acetone, warm the sample, and re-centrifuge. Add 150 mL of water, shake the sample, and check the pH. It should be above pH 8 if the soil is Na-saturated. Transfer the suspension to a 1-L shaker bottle, add 400 mL of distilled water and 10 mL of HMP (dispersant) stock solution, and shake overnight on a horizontal shaker.

15–4.2.2 SEPARATION OF THE SAND FRACTIONS

Pour the suspension through a 270-mesh (53 μm) sieve into a 1-L sedimentation cylinder. A 20-cm-diameter (8-in.) sieve is placed in a large funnel held by a stand above the cylinder. Tap the funnel gently and wash the sand thoroughly on the sieve. A soap solution placed on the sieve will aid in wetting the fine screen. Collect the washings in the cylinder. Transfer the sand to a tared beaker or aluminum weighing dish, dry (105 °C), and weigh.

Transfer the dried sand to the nest of sieves arranged from top to bottom with decreasing size in the following order: 1000-, 500-, 250-, 106-, 53-μm, and pan. Shake the sieves on a sieve shaker. A 3-min shaking time is usually adequate. Weigh each sand fraction and the residual silt and clay that passed through the 53-μm (270-mesh) sieve. Weighing precision of 0.01 g is adequate.

15–4.2.3 DETERMINATION OF SILT FRACTIONS

The 20 and 5 μm fractions can be determined by pipet by following the procedure outlined in the next section for clay and using Eq. [4] or Table 15–3 for determining the required settling times.

15–4.2.4 DETERMINATION OF CLAY (< 2 μm)

Place the cylinder containing the silt and clay suspension in a water bath; add 10 mL of HMP solution and make up to 1 L volume with distilled water; cover with a watch glass. Let the suspension stand at least several hours to equilibrate.

After equilibration, stir the suspension thoroughly with a hand stirrer for at least 30 s using an up-and-down motion. Note the time at completion of stirring and the temperature of the water bath. It is convenient to complete stirring of adjacent suspensions at intervals of about 3 min. An alternative to hand stirring is stoppering the sedimentation cylinder and shaking end-over-end for 1 min.

After the appropriate time interval (see Tables 15–1 through 15–3), lower the closed Lowy pipet carefully to the appropriate depth, turn on the vacuum, and withdraw a 25-mL sample in about 12 s (see Fig. 15–5). A device for controlling the vacuum is required.

Discharge the sample into a tared and numbered weighing bottle, beaker, or aluminum dish. Rinse the pipet with distilled water and add the rinse water to the clay suspension in the weighing bottle. Evaporate the water, dry the clay at 105 °C, cool in a desiccator, and weigh.

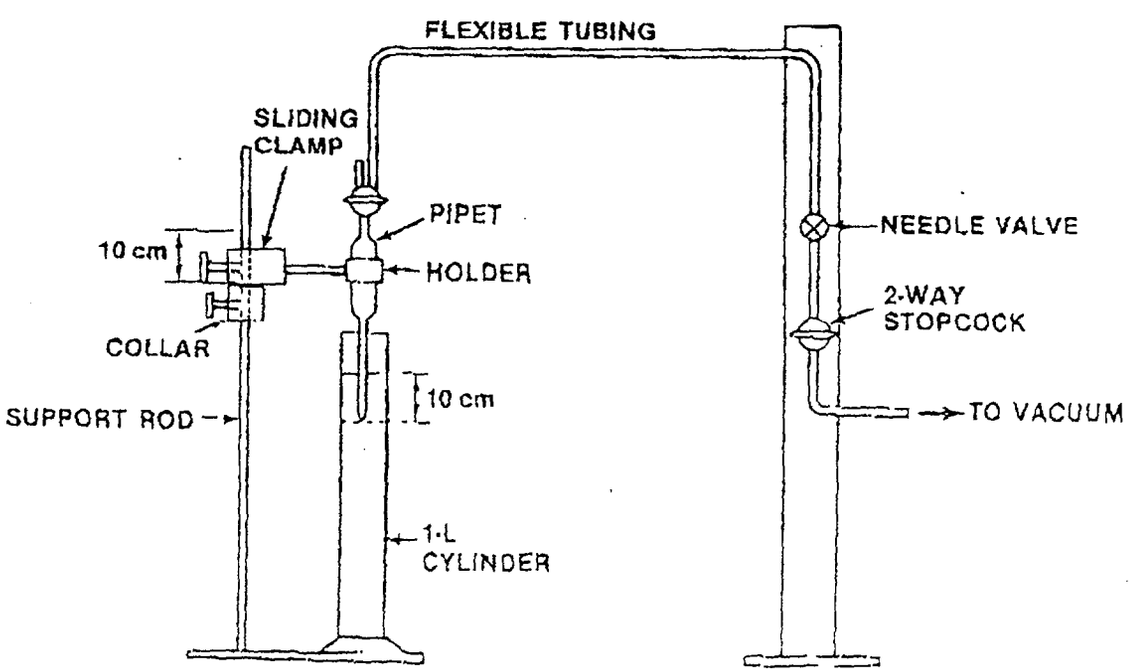


Fig. 15-5. Schematic diagram of pipet stand and apparatus for sedimentation analysis

15–4.2.5 DETERMINING THE WEIGHT OF TREATED SOIL

Add 10 mL of 1 *M* $CaCl_2$ and 1 mL of 1 *M* HCl to the suspension remaining in the cylinder to prevent $CaCO_3$ formation. Siphon off the clear solution after flocculation has occurred. Transfer the soil from the cylinder to a tared beaker, evaporate, dry at 105 °C, and weigh.

Differences between original soil weight and weight found in the cylinder are attributed to pretreatment soil loss, solution loss, sieving loss, and sample removal for pipet sieving analysis. The total oven-dry weight of the treated sample is used as the basis for calculating the size fraction. The total oven-dry weight can be expressed as:

$$W_s + W_p + W_r = W_t \qquad [12]$$

where

W_s = oven dry weight of sand fraction,
W_p = corrected oven dry weights of pipet samples,
W_r = corrected oven dry weight of residual silt and clay, and
W_t = total weight of treated sample.

W_r and W_p are corrected by subtracting the weight of the dispersing agent (Table 15–4).

15–4.3.6 Calculations

Table 15–4 shows how the pipet method is used to determine size-fraction percentages using a 25-mL pipet.

15–4.4 Comments

Flocculation of clay from suspension has been observed in soils containing large amounts of gypsum (Kaddah, 1975; Hesse, 1976; Rivers et al., 1982). Flocculation is recognized by a distinct separation of clear liquid and suspended clay (flocculated clay often has the appearance of a cloudy gel-like precipitate). Removal of soluble salts (Section 15–4.2.1.1) helps prevent flocculation in most soils. However gypsum, having a low but measurable solubility, can cause flocculation by replacement of Na

Table 15–4. Example calculations of three particle-size percentages using a 25-mL pipet.

Particle size	Sample weight	Concentration	Corrected concentration†	Percent less than‡
mm	g	g/L		%
0.020	0.114	4.56	4.06	39.8
0.005	0.073	2.92	2.42	23.7
0.002	0.067	2.28	1.78	17.4

† Dispersing agent concentration = 0.5 g/L.
‡ Based on oven-dry weight of treated sample, W_t = 10.21 g.

with Ca. Procedures for removal of gypsum are available (Rivers et al., 1982). Options for removal of gypsum include adding barium (Hesse, 1976) or increasing the concentration of HMP dispersant (Kaddah, 1975). Flocculation must be prevented for sedimentation analysis (pipet, hydrometer, etc.) to provide meaningful results.

Errors in PSA values using the pipet analysis are mainly associated with sampling and weighing. With care, clay fractions can be determined with a precision of ±1 wt% using pipet procedures.

15–5 HYDROMETER METHOD

Particle-size analysis can be done conveniently with a hydrometer which allows for nondestructive sampling of suspensions undergoing settling. The hydrometer method provides for multiple measurements on the same suspension so that detailed particle-size distributions can be obtained with minimum effort. The hydrometer method outlined is that modified from Day (1965) and ASTM (1985d).

15–5.1 Apparatus and Reagents

1. Standard hydrometer, ASTM no. 152 H, with Bouyoucos scale in g/L (Fig. 15–6).
2. Electric stirrer (malted-milk-mixer type, with 10 000-rpm motor).
3. Plunger or rubber stoppers for 1000-mL sedimentation cylinders.
4. Sedimentation cylinders with 1-L mark 36 ±2 cm from the bottom of the inside.
5. Metal dispersing cups and 600-mL beakers.
6. Amyl alcohol.
7. Sodium-hexametaphosphate (HMP) solution (50 g/L).
8. Set of sieves—7.6-cm (3 in.) diameter square mesh woven bronze wire cloth, with the following openings: 1000, 500, 250, 106, 75, and 53 μm.
9. Electric oven and weighing jars.

15–5.2 Procedure

15–5.2.1 CALIBRATION OF HYDROMETER

Add 100 mL of the HMP solution to a cylinder and make the volume to 1 L with room temperature distilled water. Mix thoroughly with plunger

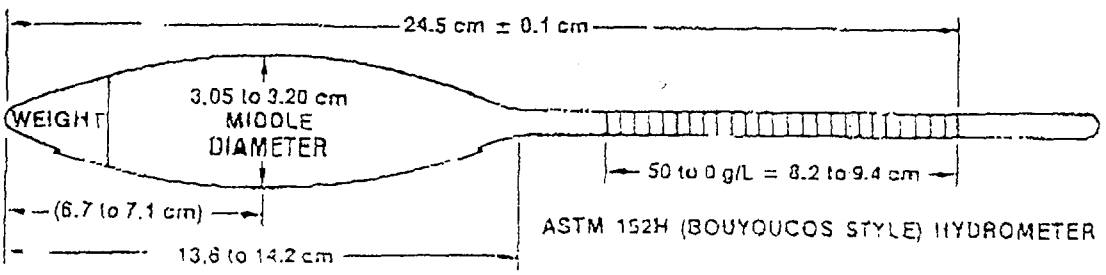


Fig. 15–6. Schematic diagram of ASTM 152 H-type hydrometer.

and record temperature. Lower the hydrometer into the solution and determine R_L, the hydrometer-scale reading of the (blank) solution. Read the upper edge of the meniscus surrounding the stem. Periodically recheck R_L during the course of the hydrometer tests (section 15–5.2.3). The calibration value R_L is used in the analysis to correct for solution viscosity and to correct the soil solution concentration, C.

15–5.2.2 DISPERSION OF SOIL

Weigh 40.0 g of soil into a 600-mL beaker, add 250 mL of distilled water and 100 mL of HMP solution, and allow the sample to soak overnight. The exact sample size depends upon soil texture. For fine-textured soils—silts or clays—10 to 20 g may be adequate. For coarse sands, 60 to 100 g will be needed in order to obtain reproducible results. Most temperate zone soils can be air dried prior to testing. However, for many tropical soils and soils of volcanic origin, samples must be stored at field moisture. Weigh another sample of the soil (about 10 g) for determination of oven-dry weight. Dry overnight at 105 °C, cool, and weigh.

Transfer the HMP-treated sample to a dispersing cup and mix for 5 min with the electric mixer, or transfer the suspension to shaker bottles and shake overnight on a horizontal shaker. Transfer the suspension to a sedimentation cylinder and add distilled water to bring the volume to 1 L.

15–5.2.3 HYDROMETER MEASUREMENTS

Allow time for the suspension to equilibrate thermally and record temperature. Insert plunger into cylinder and mix the contents thoroughly. Hold bottom of cylinder to prevent tipping. Dislodge sediment from the bottom using strong upward strokes of plunger. Finish stirring with two or three slow, smooth strokes. An alternative mixing procedure is to stopper the cylinder and use end-over-end shaking for 1 min. Add a drop of amyl alcohol if the surface of the suspension is covered with foam. As soon as mixing is completed, lower the hydrometer into the suspension and take readings after 30 s and again at the end of 1 min. Remove the hydrometer, rinse, and wipe it dry. Reinsert the hydrometer carefully about 10 s before each reading and take readings at 3, 10, 30, 60, 90, 120, and 1440 min. Times of reading can be modified according to need. Remove and clean the hydrometer after each reading. Record the reading R at each time. Read the hydrometer after placing it in the blank solution (containing no soil), and record the blank reading as R_L and the temperature at each time.

15–5.2.4 SEPARATION OF SAND FRACTIONS

Quantitatively transfer the sediment and suspension from the 1-L sedimentation cylinder through a 270-mesh (53-μm) sieve. A 20-cm-diameter (8 in.) sieve is placed over a sink. The sediment is washed onto

the 53-μm screen using a wash bottle or gentle stream of water. The 53-μm screen can be dipped in a soap solution to improve the wettability of the screen and speed the flow. Transfer the sand to a tared beaker or aluminum weighing dish, dry (105 °C), and weigh.

Transfer the dried sand to the nest of sieves arranged from top to bottom in the following order: 1000, 500, 250, 106, and 53 μm. Shake on a sieve shaker for 3 min. Weigh each sand fraction and the residual silt and clay that has passed through the 53-μm sieve.

15-5.2.5 CALCULATION OF PARTICLE SIZE

Determine C, the concentration of soil in suspension in g/L, where $C = R - R_L$, with R, the uncorrected hydrometer reading in g/L, and R_L, the hydrometer reading of a blank solution. R and R_L are taken at each time interval. Determine P, the summation percentage for the given time interval, where $P = C/C_o \times 100$ and C_o = oven-dry weight of the soil sample.

Determine X, the mean particle diameter in suspension in μm at time t, using Eq. [7], [9], and [11]:

$$X = \theta t^{-1/2}. \qquad [13]$$

For the special case that X and t are reported in μm and min, respectively, and all other terms expressed in cgs units, the sedimentation parameter is commonly written as

$$\theta = 1000(Bh')^{1/2}, \qquad [14]$$

where $B = 30\eta/[g(\rho_s - \rho_l)]$, and $h' = -0.164R + 16.3$ (Eq. [11]), and with each term expressed in the following units:[5]

θ = sedimentation parameter, μm min$^{1/2}$,
h' = effective hydrometer depth, cm,
η = fluid viscosity in poise, g cm^{-1}s^{-1},
g = gravitational constant, cm/s^2,
ρ_s = soil particle density, g/cm^3, and
ρ_l = solution density, g/cm^3.

Equations [5] and [6] can be used to provide approximate corrections for density and viscosity variations for HMP solutions.

Plot a summation percentage curve (P vs. log X) using hydrometer readings taken over a time period from 0.5 min to 24 h coupled with sieve data. From this curve determine sand, silt, and clay percentages.

For routine textural analysis a summation percentage curve has more detail than is required; hence, the following procedure may be used.

[5] The sedimentation parameter and associated terms have not been expressed in standard SI units in order to maintain consistency with reported tables (Day, 1965; Weast, 1984).

15–5.2.5.1 Simplified Clay Fraction Procedure.

1. Take hydrometer readings at 1.5 and 24 h only (record both R and R_f values).
2. Determine effective particle diameter X and summation percentage P for 1.5- and 24-h readings using Eq. [7] and [13].
3. Compute $P_{2\mu m}$ (summation percentage at 2 μm) as follows:

$$P_{2\mu m} = m \ln (2/X_{24}) + P_{24} \quad [15]$$

where

X_{24} = mean particle diameter in suspension at 24 h (from Eq. [7]),
P_{24} = summation percentage at 24 h,
$m = (P_{1.5} - P_{24})/\ln (X_{1.5}/X_{24})$ = slope of the summation percentage curve between X at 1.5 h and X at 24 h,
$X_{1.5}$ = Mean particle diameter in suspension at 1.5 h, and
$P_{1.5}$ = summation percentage at 1.5 h.

15–5.2.5.2 Sand Fraction Calculation. Compute the 50-μm summation percentage, using the same procedure as for $P_{2\mu m}$, but use the 30- and 60-s hydrometer readings rather than the 1.5- and 24-h readings, respectively, and subtract the computed $P_{50\mu m}$ value from 100 to obtain the sand percentages. A standard sieve analysis should be run for comparison, using a 53- or 47-μm screen (section 15-5.2.4).

15–5.2.5.3 Silt Fraction Calculation. Determine the percent silt by difference as

$$\% \text{ silt} = 100 - (\% \text{ sand} + \% \text{ clay}). \quad [16]$$

Calculations for sand, silt, and clay are conveniently made with a programmable desk calculator or microcomputer. BASIC and FORTRAN programs for clay fraction and textural determinations are available from the authors upon request.

15-5.2.6 COMMENTS

Flocculation of clay by soluble salts or gypsum during sedimentation may cause significant errors in the hydrometer method, since no pretreatment is used. Kaddah (1975) recommends increasing the concentration of HMP to levels high enough to maintain dispersion. If higher concentrations are used, the blank solution must contain the same concentration of HMP as that used in the soil solution so that the blank reading, R_f, corrects for the increased solution viscosity and density. If soil is high in soluble salts or gypsum, pretreatment procedures (section

15–4.2.1.1), removal techniques (Rivers et al., 1982), or chemical treatment (Hesse, 1976) may be needed.

The Bouyoucos procedure (Bouyoucos, 1962) has been used by a number of laboratories to estimate sand, silt, and clay from hydrometer measurements. Readings at 40 s and 2 h are used to estimate sand and clay percentages, respectively. From basic sedimentation theory, the 2-hr reading cannot yield correct estimates of the 2-μm clay fraction. Based on theoretical considerations, the 2-h hydrometer reading is a closer estimate of the 5-μm silt fraction than it is of the 2-μm clay fraction, and errors in clay contents using the 2-h reading often exceed 10 wt% for clay soils (Gee & Bauder, 1979). Similar problems arise when using the 40-s hydrometer reading to estimate the sand fraction. Differences between sieve and 40-s hydrometer measurement often exceed 5 wt%. The correlations between silt and clay and the 40-s and 2-h readings are empirical. In some cases, they seem adequate for textural class identification, but cannot be used to accurately define the particle size, hence, the Bouyoucos procedure is not recommended.

Walter et al. (1978) compared pipet and hydrometer measurements of 2μm size fraction in glacial till soils and found agreement well within 5%. Liu et al. (1966) also found generally good agreement between pipet and hydrometer analysis. Calculated correlation coefficients (r values) varied between 0.90 and 0.99 for 155 samples of soils from eleven states. These and other results suggest that pipet and hydrometer can give comparable results, with major differences arising largely from differences in pretreatment techniques.

A detailed error analysis for the hydrometer has been made by Gee and Bauder (1979). They indicate that the major source of error is in the hydrometer reading. An error of ± 1 g/L hydrometer reading results in an error of about ± 2 wt% for clay-size particles.

15–6 OTHER METHODS

In addition to sieving and sedimentation procedures, there are numerous techniques for measurement of particle-size distribution that have been developed for powder technology and other applications. These techniques include optical microscopy, transmission electron microscopy (TEM), scanning electron microscopy (SEM), electrical sensory zone (Coulter counter) methods, and light-scattering methods such as laser-light scattering, turbidimeters, holography, and x-ray centrifuges. An excellent discussion of these and other methods for particle-size distribution is given by Allen (1981).

Pennington and Lewis (1979) and Lewis et al. (1984) describe a procedure for using Coulter counters for particle-size distribution and textural analysis. Tama and El-Swaify (1978) have used turbidimeters to qualitatively assess clay contents in tropical soils. Weiss and Frock (1976) and Cooper et al. (1984) detail the use of laser light scattering methods

for PSA and textural analysis. Laser-light instruments normally do not operate into the clay range; hence, a correction factor is used to estimate clay-size materials (Cooper et al., 1984). Soil mineralogy, particle shape, and density all affect this correction factor.

Standard procedures for PSA using Coulter counters, turbidimeters, or laser-light techniques are not proposed at this time. High cost of instrumentation coupled with uncertainties in correction factors make these methods less attractive than the pipet or hydrometer methods for most routine applications. However, in such applications as the analysis of runoff sediments, where great numbers of tests are required, the speed of these methods has encouraged their use, particularly when only relative values of particle size are considered adequate.

15-7 REFERENCES

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MINERALOGY
INSTRUMENTAL ANALYSES (7A)
X-RAY DIFFRACTION (7A2)
PHILLIPS XRG-300 X-RAY DIFFRACTOMETER
THIN FILM ON GLASS, RESIN PRETREATMENT II (7A2i)
(Mg Room Temp, Mg Glycerol Solvated, K 300°C, K 500°C)

1. APPLICATION

Clay fractions of soils are commonly composed of mixtures of one or more phyllosilicate minerals together with primary minerals inherited directly from the parent material (Whittig and Allardice, 1986). Positive identification of mineral species and quantitative estimation of their proportions in these polycomponent systems usually require the application of several complementary qualitative and quantitative analyses (Whittig and Allardice, 1986). One of the most useful methods to identify and to make semiquantitative estimates of the crystalline mineral components of soil is X-ray diffraction analysis.

The operational strategy at the SSL and the preceding Lincoln Soil Survey Laboratory has been to adjust instrumental parameters to keep peak intensity of a soil reference constant from 1964 to present through the evolution of instrumentation. The intent is to keep the same quantitative interpretations consistent from sample to sample.

2. SUMMARY OF METHOD

Soils are dispersed and separated into fractions of interest. Sands and silts are mounted on glass slides as slurries or on double sticky tape for analysis. Clay suspensions are placed on glass slides to dry and to preferentially orient the clay minerals. The soil clay minerals of greatest interest are phyllosilicates, e.g., kaolinite, mica (illite), smectite, vermiculite, hydroxy-interlayered vermiculite, and chlorite.

Generally, no two minerals have exactly the same interatomic distances in three dimensions and the angle at which diffraction occurs is distinctive for a particular mineral (Whittig and Allardice, 1986). These interatomic distances within a mineral crystal result in a unique array of diffraction maxima, which help to identify that mineral. When several minerals are present in a sample, species identification is usually accomplished most easily and positively by determining the interatomic spacings that give rise to the various maxima and by comparing these with known spacings of minorals (Whittig and Allardice, 1986).

X-ray diffraction produces peaks on a chart that correspond to 2θ angles on a goniometer. The angle of incidence of the goniometer is relative to the surface plane of the sample. Standard tables to convert θ or 2θ angles to crystal "d" spacings are published in the U.S. Geological Survey Circular 29 (Switzer et al., 1948) and in other publications (Brown, 1980). At the SSL, conversions are made by the analysis program on the Philips diffractometer, d-spacings are recorded on an IBM-compatible 486 DOS-based computer system, and hard copies are printed for interpretation and filing. The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law as follows:

$$n\lambda = 2d \sin \theta$$

where:
- n = order of diffraction (integer)
- λ = x-radiation wavelength (Angstroms, A)
- d = crystal "d" spacing (A)
- θ = angle of incidence

When n = 1, diffraction is of the first order. The wavelength of radiation from an X-ray tube is constant and characteristic for the target metal in the tube. Copper radiation (CuKa) with a wavelength of 1.54 A (0.154 nm) is used at the SSL. Because of similar structures of layer silicates commonly present in soil clays, several treatments which characteristically affect the "d" spacings are necessary to identify

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components. At the SSL, four treatments are used, i.e., Mg^{2+} (room temperature); Mg^{2+}-glycerol (room temperature); K^+ (300°C); and K^+ (500°C).

3. INTERFERENCES

Intimate mixtures of similar phyllosilicate minerals on a fine scale cause problems in identification. The mixtures, differences in crystal size and purity, and background or matrix interferences affect quantification. No pretreatments other than dispersion with sodium hexametaphosphate are used for separation and isolation of the crystalline clay fraction. Impurities such as organic matter and iron oxides may act as matrix interferences causing peak attenuation during X-ray analysis or may interfere with clay dispersion and separation. The separation procedure to isolate the clay fraction from the other size fractions of the soil skews the <2-µm clay suspension toward the fine clay, but it minimizes the inclusion of fine silt in the fraction. Dried clay may peel from the XRD slide. One remedy is to rewet the peeled clay on the slide with 1 drop of glue-water mixture (1:7). Other remedies are as follows:

a. Place double sticky tape on the slide prior to adding the dried clay.

b. Dilute the suspension by half, if thick.

c. Crush with ethanol and dry, and then add water to make a slurry slide.

d. Roughen the slide surface with a fine grit sand paper.

Sufficient glycerol on the slides is required to solvate the clay, i.e., to expand smectites to 18 A. X-ray analysis should be performed 1 to 2 days after glycerol addition. If excess glycerol is applied to the slide and free glycerol remains on the surface, XRD peaks are attenuated. Some suggestions to dry the slides and achieve optimum glycerol solvation are as follows:

a. Use a desiccator to dry slide, usually when the clay is thin.

b. If the center of slide is whitish and dry, usually with thick clay, brush slide with glycerol or add an additional drop of glycerol.

4. SAFETY

Operate the centrifuge with caution. Keep the centrifuge lid closed when in operation. Ensure that all hangers and tubes are seated firmly in proper location. Use tongs and appropriate thermal protection when operating the muffle furnace. The diffraction unit presents an electrical and radiation hazard. Analysts must receive radiation safety training before operating the equipment. Employees must wear a radiation film badge while in the room when the diffraction unit is in operation.

5. EQUIPMENT

5.1 Teaspoon (5 g)
5.2 Dispenser, 5 mL, for sodium hexametaphosphate solution
5.3 Centrifuge, International No. 2, with No. 240 head and carriers for centrifuge tubes, International Equip. Co., Boston, MA
5.4 Centrifuge tubes, plastic, 100 mL, on which 10-cm solution depth is marked
5.5 Rubber stoppers, No. 6, for centrifuge tubes
5.6 Mechanical shaker, reciprocal, 120 oscillations min^{-1}

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5.7 Plastic cups, 60 mL (2 fl. oz.) with lids
5.8 Label machine
5.9 Hypodermic syringes, plastic, 12 mL, with tip caps
5.10 Screen, 80 mesh, copper
5.11 Dropper bottle, plastic, 30 mL (1 fl. oz.), for a 1:7 glycerol:water mixture
5.12 Muffle furnace
5.13 X-ray diffractometer, Philips XRG-300, with PW-1170 automated sample changer
5.14 PC-APD, Philips, software for Automatic Powder Diffraction (PW-1877), Version 3.5
5.15 Computer, IBM-compatible 486, Gateway 2000 4D X2-66V
5.16 Printer, Hewlett Packard LaserJet IV
5.17 Plotter, Hewlett Packard 7550 Plus
5.18 XRD slides, glass, 14 x 19 mm
5.19 XRD sample preparation board, wood, with 32 places for glass XRD slides
5.20 Slide holder. Accepts 14 x 19 mm XRD glass slides. Modified so slide surfaces rest flush with surface of holder.
5.21 Magazine for slide holder, 35 positions
5.22 Reference slides: quartz and clay from reference soil

6. REAGENTS

6.1 Distilled deionized (DDI) water
6.2 Sodium hexametaphosphate solution. Dissolve 35.7 g of sodium hexametaphosphate $(NaPO_3)_6$ and 7.94 g of sodium carbonate (Na_2CO_3) in 1 L DDI water.
6.3 Potassium chloride (KCl), 1.0 *N*. Dissolve 74.60 g KCl in 1 L DDI water or 671.40 g KCl in 9 L DDI water.
6.4 Magnesium chloride ($MgCl_2$), 1.0 *N*. Dissolve 47.61 g $MgCl_2$ in 1 L DDI water or 428.49 g $MgCl_2$ in 9 L DDI water.
6.5 Glycerol:water mixture (1:7). Add 4 mL of glycerol to 28 mL DDI water plus 2 drops of toluene.
6.6 Exchange resin, Rexyn 101 (H), analytical grade. Pretreatment of resin as follows:
6.6.1 Divide equally Rexyn 101 (H), approximately 250-g portions, into two 600-ml beakers labelled K and Mg and add appropriate salt solution (1.0 *N* KCl or 1.0 *N* $MgCl_2$). Cover resin with salt solution.
6.6.2 Stir, let settle for 10 min, decant clear solution, and add salt solution. Repeat 3 times. Leave resin covered in salt solution for 8 to 12 h.
6.6.3 Repeat step 6.6.2 second day. Resin is ready for syringes. Saturated resin not used initially for syringes can be saved for future use.
6.7 White glue, diluted 1:7 with DDI water

7. PROCEDURE

Preparation (Recharge) of Resin-Loaded Syringes

7.1 Place a small circle of 80-mesh screen in a 12-mL syringe and add 4 cm^3 of exchange resin from which salt solution has been drained. Our procedure requires each sample to have 2 Mg and 2 K slides prepared, so we produce our syringes in sets of two.

7.2 Saturate the resin in each of the four syringes with 4 mL of the appropriate 1.0 *N* salt solution ($MgCl_2$ or KCl) and expel. Repeat saturation of resin.

7.3 Fill syringe completely with the salt solution and allow to equilibrate for 4 to 20 h.

7.4 Rinse syringe twice with 4 mL of DDI water and rinse tip cap.

7.5 Completely fill syringe with DDI water and allow to equilibrate for 4 to 20 h.

7.6 Rinse syringe twice with DDI water.

7.7 Expel water, cap syringe, and store.

Preparation of Clay Suspension

7.8 Place ≈ 5 g (1 tsp) of air-dry <2-mm soil in a 100-mL plastic centrifuge tube. If the sample appears to be primarily sand, use 10 g (2 tsp) of <2-mm soil to obtain sufficient clay.

7.9 Add 5 mL of sodium hexametaphosphate solution. If the soil contains gypsum or is primarily calcium carbonate, use 10 mL of sodium hexametaphosphate dispersing agent.

7.10 Fill tube to 9.5-cm height with DDI water.

7.11 Place rubber stopper in tube and shake overnight in mechanical shaker.

7.12 Remove stopper from tube and rinse stopper and sides of tube with enough water to bring the volume to the 10-cm mark.

7.13 Balance the pairs of tubes and place in centrifuge. Centrifuge at 750 rpm for 3.0 min.

7.14 If the clay is dispersed, carefully decant 30 mL of suspension into a labelled, 60-mL, plastic cup. Place cap on cup.

7.15 If the clay did not disperse after being shaken overnight, remove the rubber stopper and carefully decant the clear supernatant liquid.

7.16 Add an additional 10 mL of sodium hexametaphosphate dispersing agent to sample and then add DDI water to 9.5-cm depth.

7.17 Stopper and shake overnight to disperse the clay. Rinse stopper and fill tube to 10-cm mark.

7.18 Centrifuge, decant, and store clay suspension.

7.19 Use the clay suspension for X-ray diffraction analysis and HF plus aqua regia dissolution analysis. Dry clay suspension for use in thermal analysis.

Thin Film on Glass, Resin Pretreatment

7.20 The SSL uses a sample board which holds 32 slides, i.e., 8 samples x 4 treatments. Prepare the sample board with glass XRD slides to receive the following 4 treatments per clay suspension sample.

Mg^{2+} - room temperature
Mg^{2+} - glycerol (room temperature)
K^{+} - 300°C (heated for 2 h)
K^{+} - 500°C (heated for 2 h)

7.21 Place one small drop of the glycerol:water mixture (1:7) on each Mg^{2+}-glycerol slide.

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7.22 Draw 1 mL of <2-µm clay suspension into the resin-loaded syringe and invert back and forth to facilitate cation exchange.

7.23 Dispense 3 drops to clear the tip.

7.24 Dispense ≈ 0.1 mL (6 to 10 drops) to cover the appropriate XRD slide. Draw DDI water into the syringe and expel 3 times to remove all of the clay suspension. Recharge the syringe after 10 times of use.

7.25 When the clay suspension has dried, transfer the slides with the K^+-saturated clays to transite plates and heat for a minimum of 2 h in a muffle furnace.

7.26 Heat the following sample slides on the XRD sample board.

K^+-300°C - slides 3, 7, 11, 15, 19, 23, 27, and 31

K^+-500°C - slides 4, 8, 12, 16, 20, 24, 28, and 32

7.27 After heating, remove the transite plate from the furnace, cool to air temperature, and return slides to XRD sample board.

X-ray Diffraction Operation

7.28 The X-ray analysis of the glycerol slide must be done within 1 to 2 days after the slide dries. If this is not possible, skip Step 7.21 when slide is prepared. Add one small drop of glycerol:water mixture (1:7) to dry slide 24 h prior to X-ray analysis.

7.29 Transfer the slides (1 to 32) from XRD sample board to slide holders (1 to 32) and place in slots (1 to 32) in a magazine for the automated sample changer.

7.30 Analyze one reference soil sample in each run. Place this sample in slot 33.

7.31 Analyze one quartz standard for 2θ and intensity calibrations in each run. Place this sample in slot 34. Intensity is measured at peak maximum at or near 26.66° 2θ for 10 s.

7.32 The 32 samples from one XRD board constitute one run on the diffraction unit. Prepare a run sheet for samples on each XRD sample board. Refer to example run instruction (7.33). Refer to Appendix XX and the manufacturer's manual for operation of the X-ray diffractometer.

7.33 Place the magazine in the automated sample changer. Confirm that the XRD shutter is off when changing magazines. Set the XRD unit parameters as follows:

CuKa radiation, λ:	1.54 A (0.154 nm)
Scan range:	2° to 34° 2θ
Generator settings:	40 kv, 20 ma
Divergence slit:	1°
Receiving slit:	0.2 mm
Monochrometer:	Yes

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Step size and scan speed vary depending on intensity of X-rays generated from tube. Adjust settings to maintain same long-term peak intensities on standard reference clay and quartz standard regardless of tube intensities.

7.34 Enter run instruction from the keyboard. Create a batch file for the automated run. File names specified are of the sample number. An example run instruction is as follows:

Batch File Name: Project number (e.g., CP95LA022)

Raw Data File Name: Run number

First Sample: 1

Last Sample: 33
(reference soil clay)

7.35 Activate program. The run stores raw data on the hard disk under the subdirectory designated by project type and year, e.g., CP95. Refer to example run instruction (7.34).

7.36 Print a hard copy of the "Detected Peaks File" for each sample and perform level 1 smoothing on diffraction patterns.

7.37 Prepare and print a 4-color graphics chart. The 4 colors are blue (Mg^{2+}); green (Mg^{2+}-glycerol); pink (K^+ 300°C); and red (K^+ 500°C). Stamp chart with label; enter run parameter information, and complete soil information, e.g., soil name, horizon designation, and depth. File hard copies of detected peaks and graphics chart in pasteboard binders by state, county, and chronology.

7.38 Record "d" spacing and intensity of quartz standard in the logbook. Record the peak intensities for designated peaks for the reference soil clay.

7.39 File the detected peaks printout and graph for the reference soil in the reference soil-clay folder.

Interpretation of X-ray Diffraction Data

7.40 The angle in degrees two theta (2θ) measured in X-ray diffraction analyses is converted to angstroms (A) using tables compiled according to Bragg's Law. Refer to summary of method. Angstroms convert to nanometers (nm) by a factor of 0.1, e.g., 14 A = 1.4 nm.

7.41 Use the following X-ray diffraction criteria to identify some common crystalline minerals. The reported "d" values are for 00*l* basal spacings. The Miller index (*hkl*) specifies a crystal face which has some orientation to the three crystallographic axes of a, b, and c. The Miller index (00*l*) indicates a crystal face that is parallel to the a and b axes, e.g., phyllosilicate minerals. The following X-ray diffraction criteria also has some questions (Q) that may aid the analyst in interpreting the diffraction patterns. These questions are a suggested procedural approach to help the analyst identify the relative locations of a few peaks and to confirm key criteria.

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(Mg Room Temp, Mg Glycerol Solvated, K 300°C, K 500°C)

X-Ray Diffraction Criteria

1. Kaolinite and Halloysite
a. Crystal structure missing at 500°C.
b. 7 A (7.2 to 7.5 A) with all other treatments
Q. Is there a 7 A peak? Is it destroyed at 500°C? Kaolinite or Halloysite.
Q. Is the peak sharp and at ~ 7.1 A? Kaolinite.
Q. Is the peak broad and at 7.2 to 7.5 A? Halloysite.

2. Mica (Illite)
a. 10 A with all treatments.
b. 10 A with Mg^{2+}-saturation
Q. Is there a 10 A peak with Mg^{2+}-saturation? Mica (Illite).

3. Chlorite
a. Crystal structure of Fe-chlorites destroyed at 650 to 700°C.
b. 14 A with all other treatments.
c. 14 A at 500°C.
d. Generally also has strong 7 A peak.
Q. Is there a 14 A peak when heated to 500°C? Chlorite.

4. Vermiculite
a. 14 A with Mg^{2+}-saturation.
b. 14 A with Mg^{2+}-glycerol solvation.
c. Nearly 10 A with K^{+}saturation.
d. 10 A when K^{+}-saturated and heated to 300°C.
Q. Is there an enhanced 10 A peak with K^{+}-saturation in comparison to Mg^{2+}saturation that cannot be attributed to smectitle? Vermiculite.

5. Smectite
a. 14 A with Mg^{2+}-saturation
b. 12 to 12.5 A with K^{+}- or Na^{+}-saturation.
c. 17 to 18 A with Mg^{2+}-glycerol solvation.
d. 10 A with K^{+}-saturation and heating to 300°C.
Q. Is there a 17 to 18 A peak upon solvation? Smectite.

6. Gibbsite
a. Peak at 4.83 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

7. Goethite
a. Peak at 4.18 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

8. Hydroxy-Interlayed Vermiculite or Smectite
a. Incomplete collapse to 10 A of smectite or vermiculite when K^{+}-saturated and heated to 300°C.

9. Quartz
a. Peaks at 4.27 A and 3.34 A with all treatments (only 3.34 if small amounts).

10. Lepidocrocite
a. Peak at 6.2 to 6.4 A with Mg^{2+} and Mg^{2+}-glycerol but destroyed when heated to 300°C.

11. Potassium Feldspar
a. Peak at 3.24 A with all treatments.

12. Plagioclase Feldspar
a. Twin peaks between 3.16 and 3.21 with all treatments.

13. Calcite
a. Peak at 3.035 A with all treatments.

14. Dolomite
a. Peak at 2.88 to 2.89 A with all treatments.

15. Gypsum
a. Peak at 4.27 A with Mg^{2+} and Mg^{2+}-glycerol, but destroyed when heated to 300°C.

16. Mixed Layer Vermiculite-Mica
a. Peak at 11 to 13 A with Mg^{2+} that does not expand with Mg^{2+}-glycerol.
b. Peak collapses to 10 A with K^{+}-saturation and heating to 300°C.

17. Mixed Layer Smectite-Mica
a. Peak at 11 to 13 A with Mg^{2+} that expands to 14-16 A with Mg-glycerol.
b. Peak collapses to 10 A with K^{+}-saturation and heating to 300°C.

18. Mixed Layer Chlorite-Mica
a. Peak at 14 A with Mg^{2+} and Mg^{2+}-glycerol.
b. Peak collapses toward 10 A with K^{+}-saturation and heating to 300°C, and more completely with heating to 500°C, but never to 10 A.

19. Mixed Layer Chlorite-Smectite
a. Peak at 11 to 13 A with Mg^{2+}-saturation that expands to about 16 A with Mg^{2+}-glycerol.
b. Collapses to about 12 A with K^{+}-saturation and heating to 300°C and 500°C.

7.42 Use the X-ray diffraction criteria, i.e., diagnostic basal 00/ spacings (A), in Table 1 for identification and ready reference of some common crystalline minerals as affected by differentiating sample treatments.

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Table 1. X-ray diffraction parameters of common soil clay minerals.

Mineral	Treatment						
	Na^+	Mg^{2+}	Mg^{2+} Gly	K^+	K^+ 300°C	K^+ 500°C	K^+ 700°C
	00/ diffraction spacing in angstroms						
Kaolinite	7	7	7	7	7	LD[2/]	LD
Halloysite	7B[2/]	7B	7B	7B	7B	LD	LD
Mica (Illite)	10	10	10	10	10	10	10
Chlorite	14*[3/]	14*	14*	14*	14*	14*	T[4/]
Vermiculite	14	14	14	10	10	10	10
Smectite	12.5	14	18	12.5	10	10	10
Gibbsite	4.85	4.85	4.85	4.85	LD	LD	LD
Goethite	4.18	4.18	4.18	4.18	LD	LD	LD
Interlayer	10-14	10-14	10-18	10-14	10-14	10-14	10-14
Quartz	3.14 and 4.27 for all treatments						
Calcite	3.035 for all treatments						
Dolomite	2.88 for all treatments						

[1/] LD = Lattice destroyed
[2/] B = Broad peak is common
[3/] * = Sometimes <14A
[4/] T = Temperature of decomposition varies with chemical composition, particle-size, and heating conditions.

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7.43 Preferential orientation of clay mineral samples enhances diffraction from the basal (00*l*) spacing and tends to minimize the number and intensity of peaks from diffraction by other *hkl* planes. With preferential orientation, second, third, and fourth order peaks may be recorded in addition to the basal first order peaks. Groups of associated peaks that differ by order of diffraction are as follows:

Smectite (Mg^{2+}-glycerol):
a. 17 to 18 A.
b. 8.5 to 9 A (weak).

Chlorite, vermiculite, and smectite:
a. 14, 7, 4.7, and 3.5 A.
b. 7, 4.7, and 3.5 A weak for smectite.

Mica:
a. 10, 5 (weak in biotites and moderate in muscovites), and 3.3 A.

Kaolinite:
a. 7 and 3.5 A.

7.44 The differentiation of kaolinite and halloysite in a sample can be aided by the use of formamide (Churchman et al., 1984). The intercalation and expansion of halloysite to a d-spacing of ≈ 10.4 A is relatively rapid (20 to 30 min), whereas kaolinite expansion requires ≈ 4 h upon treatment. The procedure is as follows:

a. Lightly spray formamide as an aerosol on the dried Mg^{2+}-saturated slide.

b. Wait 15 min but not more than 1 h and X-ray approximately 7.6 to 13.5° 2θ (d = 11.6 to 6.55 A).

c. Halloysite will expand to ≈ 10.4 A, whereas kaolinite will remain unchanged.

d. Heating the sample to 110°C for 15 min will collapse the halloysite to ≈ 7 A.

e. The total amount of kaolinite and halloysite can be determined by thermal analysis. The intensity ratio of the 10.4 to 7.2 A peaks of the formamide-treated sample can be used to determine the relative percentage of halloysite and kaolinite.

8. CALCULATIONS

X-ray diffraction produces peaks on a chart that corresponds to 2θ angle on a goniometer. Standard tables to convert θ or 2θ to crystal "d" spacings are published in the U.S. Geological Survey Circular 29 (Switzer et al., 1948) and in other publications (Brown, 1980). The crystal "d" spacings of minerals, i.e., the interval between repeating planes of atoms, can be calculated by Bragg's Law. Refer to summary of method.

9. REPORT

From the "Detected Peaks File" and graphics chart, identify the minerals present according to the registered "d" spacings. As a first approximation, use the following peak intensities, i.e., peak

heights above background in counts s^{-1}, to assign each layer silicate mineral to one of the 5 semiquantitative classes.

Class	Peak Height above Background (counts sec^{-1})
5 (Very Large)	>1.88 X 10^3
4 (Large)	1.12 to 1.88 X 10^3
3 (Medium)	0.36 to 1.12 X 10^3
2 (Small)	0.11 to 0.36 X 10^3
1 (Very Small)	<0.11 X 10^3

Adjust class placement to reflect area under the curve if peak is broad relative to peak height or if thermal, elemental, clay activity data, or other evidence warrant class adjustment. If there are no peaks or no evidence of crystalline components, place the sample in NX class (noncrystalline).

10. PRECISION

Precision data are not available for this procedure. Procedure 7A2i (X-ray diffraction) is semiquantitative.

11. REFERENCES

Brown, G. 1980. Appendix I (Tables for the determination of d in A from 2θ for the KA and KB radiations of copper, cobalt, and iron). *In* G.W. Brindley and G. Brown (eds.) Crystal structures of clay minerals and their x-ray identification. Mineralogical Soc. Monograph No. 5. Mineralogical Soc. Great Britain. pp 439-475.

Churchman, G.J., J.S. Whitton, G.G.C. Claridge, and B.K.G. Theng. 1984. Intercalation method using formamide for differentiating halloysite from kaolinite. Clays and Clay Minerals. 32:241-248.

Switzer, G., J.M. Axelrod, M.L. Lindberg, and E.S. Larsen 3d. 1948. U.S. Dept. Interior. Geological Survey. Circular 29. Washington, DC.

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CHEMICAL CHARACTERISTICS SOPs

A.5 Metals Speciation, and Quantification of Perlite

A.6 *In Vitro* Test Method

Date: September 3, 1999 (Rev. # 0) SOP No. ISSI-VBI70-09

Title: METAL SPECIATION AND QUANTIFICATION OF PERLITE

APPROVALS:

Author: ISSI Consulting Group, Inc. Date: _____

SYNOPSIS: A standardized method for speciating metals and perlite particles in solid samples is described. Equipment operating conditions, sample preparation and handling, and statistical equations for data analysis and presentation are included.

REVIEWS:

TEAM MEMBER	SIGNATURE/TITLE	DATE
USEPA Region 8	/RPM	9/10/99
ISSI Consulting Group, Inc.	WS Bratton	9/13/99

1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to specify the proper methodologies and protocols to be used during metal speciation of various solid samples (including tailings, slags, sediments, dross, bag house dusts, and paint), residential soils and dusts for metals. The metal speciation data generated from this SOP may be used to assess the solid samples as each phase relates to risk. Parameters to be characterized during the speciation analyses include particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. In addition, aliquots of solid samples can be analyzed separately for perlite. using the same methodology. Perlite particles are counted and sized based on the mineral constituents of each particle. This electron microprobe (EMP) technique, instrument operation protocols and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date, numerous metal-bearing forms of soils have been identified from various environments within western mining districts (Table 2-1) (Emmons et al., 1927; Drexler, 1991 per. comm.; Drexler, 1992; Davis et al., 1993; Ruby et al., 1994; CDM, 1994; WESTON, 1995). This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms are minerals with varying metal concentrations (e.g., lead phosphate, iron-lead oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (e.g., lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It may be important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 microns (μm) are most available for human ingestion and/or inhalation (Bornschein, et al., 1987). For this study, the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined. It has been shown (CDM, 1994) that data collected on particle area produces similar results. These measurements add a considerable amount of time to the procedure and limit the total number of particles or samples that can be observed in a study.

Mineral association may have profound effects on the ability for solubilization. For example, if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix, the two samples are likely

to pose significantly different risk levels to human health. Therefore, associations of concern include the following:

1) free or liberated
2) inclusions within a second phase
3) cementing
4) alteration rims

3.0 SAMPLE SELECTION

Samples should be selected and handled according to the procedure described in the Project Plan.

4.0 SCHEDULE

A schedule for completion of projects performed under this Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder or other comparable facilities. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the TN-5600 data processing system. RJ Lee ZEPPELIN and DATALINK hardware may be used for image storage and processing. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses will be used.

6.0 PRECISION AND ACCURACY

The precision of the EMP speciation will be evaluated based on sample duplicates analyzed at a frequency of 10%. The accuracy of the analyses will be estimated based on a number of methods, depending on the source of the data. Data generated by the "EMP point count" will be evaluated statistically based on the methods of Mosimann (1965) at

the 95% confidence level on the frequency data following Equation 1.

$$E_{0.95} = 2P(100-P)/N \qquad \text{(Eq. 1)}$$

Where: $E_{0.95}$ = Probable error at the 95% confidence level

P = Percentage of N of an individual metal-bearing phase based on percent length frequency

N = Total number of metal-bearing grains counted

For arsenic, the goal is to count 200 particles and the goal for lead is to count 100 particles. In the event that these goals are achieved in less than 8 hours, particle counting of Pb and As will be discontinued but counts of the other target metals (Cd, Zn, In, Tl, Se, Hg and Sb) will continue until the 8 hours has expired. NIST 2710 or 2711 "Montana soils" will be speciated for traceability.

Quantitative elemental analysis, primarily performed on slag or other variable, metal-bearing forms, will have precision and accuracy evaluated on counting statistics and reproducibility of NIST or other certified standards using conventional EMP methods. In general, site-specific concentrations for these variable, metal-bearing forms will be determined by performing "peak counts" on the appropriate wavelength spectrometer. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced databases or estimated based on similar compounds.

7.0 PERSONNEL RESPONSIBILITY

The analysts will carefully read this SOP prior to any sample examination.

It is the responsibility of the laboratory supervisor and designates to ensure that these procedures are followed, to examine quality assurance (QA) and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the contractor.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses sheets (DAS), will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the contractor representative of any problems encountered in the sample analysis process.

8.0 METHODOLOGY

8.1 Sample Preparation

Grain mounts, 1.5 inches in diameter, of each sample will be prepared using air-cured epoxy. The grain mounting is performed as follows:

1) Log the samples for which polished mounts will be prepared.

2) Inspect all disposable plastic cups, making sure each is clean and dry.

3) Label each "mold" with its corresponding sample number.

4) All samples will be split to produce a homogeneous 1-4 gram sample.

   NOTE: Separate splits for perlite must be prepared.

5) Mix epoxy resin and hardener according to manufacturer's directions.

6) Pour 1 gram of sample into mold. Double check to make sure sample numbers on mold and the original sample container match. Pour epoxy into mold to just cover sample grains.

7) Use a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.

8) Set molds to cure at ROOM TEMPERATURE in a clean restricted area. Add labels with sample numbers and cover with more epoxy resin. Leave to cure completely at room temperature.

9) One at a time remove each sample from its mold and grind flat the back side of the mount.

10) Use 600 grit wet abrasive paper stretched across a grinding wheel to remove the bottom layer and expose as many mineral grains as possible. Follow with 1000 grit paper.

NOTE: perlite samples should be mounted on glass thin sections prior to polishing. Perlite particle counts should be counted under polarized transmitted light.

11) Polish with 15 um oil-based diamond paste on a polishing paper fixed to a lap. Use of paper instead of cloth minimizes relief.

12) Next use 6um diamond polish on a similar lap.

13) Finally polish the sample with 1um oil-based diamond paste on polishing paper, followed by 0.05 um alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 um, 20 minutes for 6 um, 15 minutes for 1 um, and 10 minutes for 0.05 um.

NOTE: use low speed on the polishing laps to avoid "plucking" of sample grains.

14) Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and fingerprints.

15) To ensure that no particles of any metal are being cross-contaminated during sample preparation procedures, a blank (epoxy only) mold will be made every 20^{th} sample (5% of samples) following all of the above procedures. This mold will then be speciated along with the other samples.

16) Each sample must be carbon coated. Once coated, the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

8.2 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 8-2. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent per sample.

8.3 Data Presentation

Analysts will record data as they are acquired from each sample using the LEGS software, which places all data in a spreadsheet file format. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, C= cementing, R = rimming, I = included) (Figure 8-3). The analyst may also summarize his/her observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency bar-graph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size-histograms of each metal-bearing form can be constructed from data in the file.

Data from EMP will be summarized using two methods. The first method is the determination of FREQUENCY OF OCCURRENCE. This is calculated by summing the longest dimension of all the metal-bearing phases observed and then dividing each phase by the total.

Equation 2 will serve as an example of the calculation.

$$F_M \text{ in phase-1} = \frac{\Sigma (PLD)_{\text{phase 1}}}{\Sigma (PLD)_{\text{phase-1}} + \Sigma (PLD)_{\text{phase-2}} + \Sigma (PLD)_{\text{phase-n}}} \quad \text{(Eq. 2)}$$

Where:
F_M = Frequency of occurrence of metal in a single phase.
PLD = An individual particle's longest dimension
$\%F_M$ in phase-1 = F_M in phase-1 * 100

These data thus illustrate which metal-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report is the determination of RELATIVE METAL MASS. These data are calculated by substituting the PLD term in the equation above with the value of M_M. This term is calculated as defined below.

$$M_M = FM * SG * ppm_M \quad \text{(Eq. 3)}$$

Where:

M_M = Mass of metal in a phase
SG = Specific Gravity of a phase
ppm_M = Concentration in ppm of metal in a phase

The advantage in reviewing the RELATIVE METAL MASS determination is that it gives one information as to which metal-bearing phase(s) in a sample are likely to control the total bulk concentration for a metal of interest. For example, PHASE-1 may comprise 98% relative volume of the sample; however, it has a low specific gravity and contains only 1,000 parts per million (ppm) arsenic. PHASE-2 comprised 2% of the sample, has a high specific gravity, and contains 850,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

Finally, a concentration for each phase is calculated. This quantifies the concentration of each metal-bearing phase. This term is calculated as defined below (Eq. 4).

$$ppm_M = M_M * \text{Bulk metal concentration in ppm} \quad \text{(Eq. 4)}$$

8.4 Analytical Procedure

A brief visual examination of each sample will be made, prior to EMP examination. This examination may help the operator by noting the occurrence of slag and/or organic matter. Standard operating conditions for quantitative and qualitative analyses of metal-bearing forms are given in Table 8-1. Quality control will be maintained by analyzing standards and duplicates at regular intervals (Section 8.5).

The backscattered electron images will be examined using two settings: one for light-element matrices (slag or organic) and the second for heavy-element matrices (lead sulfide or lead carbonate etc.). This procedure will minimize the possibility that metal-bearing minerals may be overlooked during the scanning of the polished grain mount. The scanning will be done manually in a manner similar to that depicted in Figure 8-2. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 um) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the

particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on a EMP, with spectrometers peaked at sulfur, oxygen, carbon and the metal of concern (M). The size of each metal-bearing phase will be determined by measuring in microns the longest dimension.

As stated previously, a maximum of 8 hours will be spent in scanning and analyzing each mount. For arsenic, the goal is to count 200 particles and the goal for lead is to count 100 particles. In the event that these goals are achieved in less than 8 hours, particle counting of Pb and As will be discontinued but counts of the other target metals (Cd, Zn, In, Tl, Se, Hg and Sb) will continue until the 8 hours has expired. NIST 2710 or 2711 "Montana soils" will be speciated for traceability.

Perlite distribution will be examined under polarized transmitted light, and will be counted according to particle size and chemical constituents. Perlite particles will be sorted according to the presence of the following minerals:

Si
Si-Al
Si-Al-Fe
Si-Al-Ca-Fe

Quantitative Analyses

Quantitative analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents as: Iron-(M) sulfate, Iron-(M) oxide, Manganese-(M) oxide, organic, and slag. These determinations are important, especially in the case of slag, which is expected to have considerable variation in their dissolved metal content. Results will be analyzed statistically to establish mean values. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the later case, non-parametric statistics may have to be used or the median value has to be established.

Associations

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes. A positive/negative, black and white film (Polaroid 55) will be used or a 128x128 (minimum) binary image in ".tif" format may be stored. Recorded on each

photomicrograph and negative will be a scale bar, magnification, sample identification and phase identification. Abbreviations for the identified phases should be used. Examples are listed in Table 8-2. A final list must be submitted with the laboratory report.

8.5 Instrument Calibration and Standardization

The WDS will have spectrometers calibrated for the metal of concern, carbon, oxygen and sulfur on the appropriate crystals using mineral standards. The EDS will have multi-channel analyzer (MCA) calibrated for known peak energy centroids. Calibration will be performed so as to have both low (1.0-3.0 KeV) and high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

The magnification marker on the instrument will be checked once a week. This will be performed by following manufacturer instructions or by measurement of commercially available grids or licite spheres. Size measurements must be within 4 microns of certified values.

Initial calibration verification standards (ICVs) must be analyzed at the beginning of each analytical batch or once every 24 hours, whichever is more frequent. A set of mineral or glass standards will be run quantitatively for the metal of concern, sulfur, oxygen and carbon. If elemental quantities of the ICVs do not fall within +/- 5% of certified values for each element, the instrument must be recalibrated prior to analysis of investigative samples.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5-second EDS spectra is collected and peaks identified. The count rates for the metal(s) of concern, sulfur, carbon and oxygen can be either visually observed on the wavelength spectrometers or K-ratios calculated.

9.0 PERSONAL HEALTH AND SAFETY

Each individual operating the KEVEX x-ray fluorescence or electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University and follow all State guidelines for operation of X-ray equipment.

Latex gloves and particulate masks will be worn during preparation of sample cups. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

10.0 FINAL REPORT

A final laboratory report will be provided to the Contractor. The report will include all EMP data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include: 1) a series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit; 2) summary histograms of metal phases identified for each waste type; 3) a summary histogram of particle size distribution in each waste type; and 4) a summary of metal phase associations. Representative photomicrographs or TIFF images will also be included in the final report.

11.0 REFERENCES

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Table 2-1

Metal-Bearing Forms Found Within Western Mining and Smelting Districts

OXIDES

- Lead Oxide
- Manganese (metal) oxide
- Iron (metal) oxide
- Lead molybdenum oxide
- Arsenic Oxide
- Cadmium Oxide
- Copper Oxides
- Zinc Oxide
- Lead Arsenate
- Arsenic Trioxide
- Calcium (metal) oxide

SILICATES

- Slag
- Lead silicate
- Arsenic silicate
- Zinc silicate
- Clays

SULFATES

- Iron (metal) sulfate
- Lead sulfate
- Lead barite
- Zinc Sulfate
- Arsenic sulfate
- Copper sulfate

CARBONATES

- Lead Carbonate
- Zinc Carbonate

PHOSPHATES

- (metal) phosphates

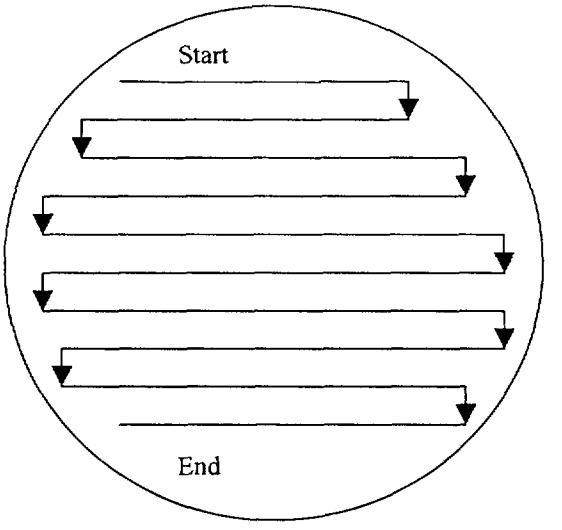
SULFIDES

- Lead sulfide
- Sulfur-containing salts
- Iron-arsenic sulfide
- Zinc sulfide
- Copper sulfides
- Copper-iron sulfide
- Cadmium Sulfide

OTHER

- Native: Lead, Copper, Cadmium, Mercury, Indium, Thallium, Selenium
- Lead/Arsenic/Cadmium/Mercury Chlorides
- Lead paint
- Solder
- Organic lead
- Lead vanadate
- Minor telluride, and bismuth-lead phases

Figure 8-2



ASSAY	_____	Pb ASSAY	_____
SAMPLE ID	_____	LAB	_____
ANALYST	_____	TIME END	_____
TIME START	_____		

Figure 8-3

NOTES	IDENTITY	SIZE		Liberated	Inclusions	Incrusted Intergrown Cemented	Rim
		Length (um)	Area (um)				

Table 8-1

EMP Standard Operating Conditions

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	NA	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF In L-alpha PET Tl L-alpha LIF Hg L-alpha LIF Se L-alpha LIF Sb L-alpha PET	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV In L-alpha 3.28 KeV Tl M-alpha 2.27 KeV Tl L-alpha 10.26 KeV Hg L-alpha 9.98 KeV Hg M-alpha 2.19 KeV Se L-alpha 1.37 KeV Sb L-alpha 3.60 KeV

Table 8-2

Suggested Abbreviation for Photomicrographs

Metal-bearing Phase	Abbreviation
In	In
Tl	Tl
Hg	Hg
Se	Se
Sb	Sb
Lead Sulfide	Ga
Lead Sulfate	Ang
Lead Carbonate	Cer
Mn-(M) Oxide	Mn(M)
Fe-(M) Oxide	Fe(M)
(M)Phosphate	(M)Phos
Fe-(M) Sulfate	Fe(M)Sul
Metal Oxide	(M)O
Pb-Mo Oxide	Wulf
Slag	Slag
Metallic Phase	(M)
Metal Silicate	(M)Si
Solder	Sold
Paint	Pnt
Metal-bearing Organic	(M)(Org)
(M) barite	(M)Bar
Pb arsenate	PbAsO
Pb vanadate	PbVan
As-Sb Oxide	AsSbO
Chalcopyrite	Cp
Sphalerite	Sph
Arsenopyrite	Apy

QUALITY ASSURANCE PROJECT PLAN

FOR EVALUATING THE

SIMPLIFIED IN VITRO TEST METHOD

PREPARED FOR:

THE SOLUBILITY/BIOAVAILABILITY RESEARCH CONSORTIUM

1.0 QUALITY CONTROL REQUIREMENTS

1.1 Elements of QA/QC

The overall purpose of this project is to determine a correlation of the in vitro test method to animal study results. QA/QC requirements will be such that this correlation can be made with sufficient confidence before general use of the method can be considered acceptable.

A standard method for the in vitro extraction of soils/solid materials is specified in SOP#1, and all participating laboratories must follow the procedure set forth in the SOP to maintain consistency throughout method validation. Specific quality control procedures prior to analysis are included in SOP #ISSI-VBI70-10. These specific QC procedures involve preparation of quality control samples for analysis and are as follows (see Table 1 for summary of QC procedures, frequency, and control limits):

Reagent Blank--Extraction fluid analyzed once per batch.

Bottle Blank--Extraction fluid only run through the complete extraction procedure at a frequency of no less than 1 per 20 samples or one per extraction batch, whichever is more frequent.

Blank Spikes--Extraction fluid spiked at 10 mg/L lead and 1 mg/L arsenic and run through the extraction procedure at a frequency of no less than every 20 samples or one per extraction batch, whichever is more frequent. Blank spikes should be prepared using traceable 1,000mg/L lead and arsenic standards in 2 percent nitric acid.

Duplicate--duplicate extractions are required at a frequency of 1 for every 10 samples. At least one duplicate must be performed on each day that extractions are conducted.

Matrix Spike--The sample used for the duplicate will also be spiked prior to extraction (10 mg/L lead and 1 mg/L arsenic) to evaluate recovery of a soluble spike in the presence of test material. Matrix spikes should be prepared using traceable 1,000 mg/L lead and arsenic standards in 2 percent nitric acid. At least one matrix spike must be performed on each day that extractions are conducted.

Standard Reference Materials--National Institute of Standards and Testing (NIST) material 2711 (Montana Soil) will be used as a laboratory control sample (LCS). The LCS will be analyzed three times during the testing of

solid/soil materials during method validation. These will be sent blind to each laboratory.

Control limits for these QC samples are delineated in the following discussion.

The laboratory should analyze all extracts by SW-846 method 6010B, December 1996 revision. The project-required detection limits (PRDLs) for lead and arsenic are 100 µg/L and 20 µg/L, respectively. Lead content of all soil/solid material should be sufficiently high that achieving these PRDLs by method 6010B should not be a problem.

TABLE 1. SUMMARY OF QC SAMPLES, ANALYSIS FREQUENCY, AND CONTROL LIMITS

QC Sample	Analysis Frequency	Control Limits
Reagent blank	once per batch	<25 µg/L lead <5 µg/L arsenic
Bottle blank	5%	<50 µg/L lead <10 µg/L arsenic
Blank spike	5%	85-115% recovery
Duplicate	10%	±20% RPD
Matrix spike	10%	75-125% recovery

Arsenic concentrations in samples tested for arsenic may not be high enough for method 6010B to detect above the PRDL. In those cases where arsenic is not detected in samples by method 6010B (ICP), analysis by either ICP-MS (method 6020, September 1994) or ICP-hydride (method 7061A, July 1992) will be required to reach the PRDL for arsenic.

Laboratories will follow all method requirements, and quality control samples listed in SOP #ISSI-VBI70-10 will be required.

1.2 QA/QC Procedures

Specific laboratory procedures and QC steps required include:

Calibration

Instruments will be calibrated according to method and instrument manufacturer. An acceptable calibration curve shall be one with a correlation coefficient of $\geq$0.995. At least one blank shall be analyzed for each calibration curve. The highest calibration standard shall not exceed the linear range of the instrument. At least one non-blank calibration standard shall be used for ICP (6010B) analyses, and method calibration requirements will be used for ICP-MS (6020) and ICP-hydride (7061A). All calibration standards and blanks should be matrix-matched with extracted samples.

Calibration Verification

Immediately following completion of a successful instrument calibration, an initial calibration verification standard (ICV) of known concentration and from an alternative source from the calibration standards will be analyzed. This standard should be in the mid-range of the calibration curve, and when analyzed, must be within 10% of the certified true value. If the ICV is not within 10% of the true value, the analyses will be terminated, any problems fixed, the instrument recalibrated, and the ICV rerun until a successful calibration and ICV are obtained. No samples shall be analyzed without a successful calibration and ICV. The ICV or another standard of known value at approximately mid-range shall be analyzed every ten samples (not counting QC samples) and be within 10% of its certified true value; this standard will be used as a continuing calibration verification (CCV) standard. If at any time, a CCV is not within 10% of its certified value, sample analyses will be terminated, problems fixed, the instrument recalibrated, and all samples since the last in-compliance CCV reanalyzed. The analytical run should end with a successful analysis of a CCV standard.

Calibration Blanks

Immediately following the ICV, an initial calibration blank (ICB) will be analyzed. This blank is made from contaminant-free deionized water (Type II) and should be matrix-matched with the extracted samples. No analytes of concern (lead or arsenic) should be detected in this blank. However, due to instrument and electronic noise, a positive or negative result within three times the standard deviation of the statistically derived detection limit is acceptable. If the ICB is outside this limit, the analysis shall be terminated, the problem fixed, the instrument recalibrated, an ICV analyzed with acceptable results, and an ICB reanalyzed. If problems persist, the possibility of contaminated glassware or reagents must be considered. Each ten samples and immediately after the CCVs, a continuing calibration blank (CCB) must be analyzed. The same acceptance criteria for the ICB apply to the CCB. If problems with the CCB occur, analysis must be terminated, problems fixed, the instrument recalibrated as described in the calibration section, and all samples since the last acceptable CCB or ICB reanalyzed. The analytical run should end with a successful analysis of a CCB

sample.

Interference Check Samples

After the ICV and ICB standards are analyzed successfully, the laboratory shall analyze an interference check sample (ICS). The laboratory may prepare the ICS as described in the ICP (6010B) or ICP-MS (6020) methods (ICS is not required for 7061A) or purchase the ICS from commercial vendors. The ICS consists of two solutions: ICSA, which contains interferents, and ICSAB, which contains interferents and analytes. Both solutions must be analyzed as described in the method. ICSA should not contain significant amounts of analyte (arsenic or lead). If the analysis of this solution results in more than three times the standard deviation around the instrument detection limit, improper interelement or background corrections should be suspected. If this happens, the analysis should be terminated, the problem fixed, the instrument recalibrated, and ICVs and ICBs reanalyzed, followed by ICSA analysis. If the problem persists, contaminated reagents and/or glassware should also be investigated. Once the ICSA is successfully analyzed, solution ICSAB shall be analyzed. All analytes of interest in the ICSAB should be within 20% of the stated true values. If not, investigation of possible interferences should begin, and any interelement or background corrections readjusted to correct the problems. The calibration and QC standards required prior to the ICSAB must be re-analyzed (meeting all QC requirements) until a successful analysis of the ICSAB solution is obtained. Once the sequence of calibration, ICV, ICB, ICSA, and ICSAB is successfully completed, sample analysis may begin.

The ICSA/ICSAB pair must also be analyzed with acceptable results at the end of the analytical run or at the end of each eight-hour shift, whichever is more frequent.

Matrix Spikes/Duplicates

Duplicate and spike sample preparation are described earlier in this section and in SOP #ISSI-VBI70-10. Duplicate results should agree within 20% relative percent difference (RPD) as defined in method 6010B. If the RPD is greater than 25% for one duplicate set, or the average RPD for the entire study is greater than 20%, samples should be thoroughly remixed and re-extracted. Matrix spike results should be in the range 75-125%. However, because these samples have not been extensively tested by this method, the expected percent recovery is not known. The laboratory should calculate spike recovery, and if any spike results are outside the 75-125% recovery range, analyze a post-extraction spike (prepared from the previously unspiked extract). This post-extraction spike should be approximately twice the amount found in the extract.

Serial Dilution

The laboratory shall take one sample (non-spiked, non-SRM, non-QC related) and perform a 1:4 serial dilution. This dilution will then be analyzed to check for possible interference (ICP method 6010B only).

Laboratory Control Sample (LCS)

The SRM NIST 2711 will be used as a laboratory control sample for this project. Sample results for lead and arsenic should fall within acceptable control limits. These samples will be submitted blind to the laboratories, and the SBRC will evaluate results from this analysis to help determine the accuracy of test results.

Reagent Blanks/Bottle Blanks/Blank Spikes

Reagent blanks must not contain more than one-fourth of the project-required detection limits (PRDLs) for arsenic and lead (i.e., less than 5 µg/L arsenic and 25 µg/L lead). Bottle blanks must not contain arsenic or lead concentrations greater than one-half the PRDLs for arsenic and lead (i.e., less than 10 and 50 µg/L of arsenic and lead, respectively). If either the reagent blank or a bottle blank exceeds these values, contamination of reagents, water, or equipment should be suspected. In this case, the laboratory must investigate possible sources of contamination and mitigate the problem before continuing with sample analysis. Blank spikes should be within 15% of their true value. If recovery of any blank spike is outside this range, possible errors in preparation, contamination, or instrument problems should be suspected. In the case of a blank spike outside specified limits, the problems must be investigated and corrected before continuing sample analysis.

Chain of Custody/Good Laboratory Practices

All samples to be tested under this study will be shipped from Region 8 EPA under chain of custody. Each participating laboratory must sign and date the chain-of-custody form when receiving samples. The laboratory must also initial and date chain-of-custody seals, which are used to seal shipping containers and ensure that custody is not broken. Copies of the signed chain-of-custody form and chain-of-custody seals must be kept. Samples must be kept under custody while in the laboratory, and custody must be documented by each laboratory. Each laboratory must follow good laboratory practices as defined in 40 CFR Part 792 to the extent practical and possible. The goal of this project is to collect scientifically credible data to determine the usefulness and implementability of this test method, and as such, laboratory data of the highest quality must be obtained.

APPENDIX A

Extraction Test Checklist Sheets

Extraction Test Checklist

I. Extraction Procedures

Extraction Fluid Preparation:

Date of Extraction Fluid Preparation:_____ Prepared by:_____
Extraction Fluid Lot #:_____

Component	Lot Number	Fluid Preparation 1L	Fluid Preparation 2L	Acceptance Range	Actual Quantity	Comments
Deionized Water		0.95 L (approx.)	1.9 L (approx.)	---		
Glycine		30.03±0.05 g	60.06±0.05g	---		
HCl [a]		60 mL (approx.)	120 mL (approx.)	---		
Final Volume	---	1 L (Class A, vol.)	2 L (Class A, vol.)	---		
Extraction Fluid pH value (@ 37°C)	---	1.50±0.05	1.50±0.05	1.45–1.55		

[a] Concentrated hydrochloric acid (12.1 N)

Extraction Test Checklist

Required Parameters:

Volume of extraction fluid (V) = 100 ±0.5 mL
Mass of test substrate (M) = 1.00 ±0.05 g
Temperature of water bath = 37 ±2 °C
Extraction time = 60 ±5 min

Extractor rotation speed = 30 ±2 rpm
Maximum elapsed time from extraction to filtration = 90 minutes
Maximum pH difference from start to finish (ΔpH)= 0.5 pH units
Spike solution concentrations: As = 1 mg/L; Pb = 10 mg/L

Date of Extraction:_____
Extraction Fluid Lot #:_____
Extracted by:_____

As Spike Solution Lot #:_____
Pb Spike Solution Lot #:_____

Extraction Log:

Sample ID	Sample Preparation		Extraction								Filtration	
	V (mL)	M (g)	Start Time[a]	End Time[a]	Elapsed Time (min)	Start pH	End pH	ΔpH	Start Temp (°C)	End Temp (°C)	Time[a]	Time Elasped from extraction (min)
Acceptance Range	(95.5-100.5)	(0.95-1.05)	---	---	(55-65 min)	---	---	(Max = 0.5)	(35-39)	(35-39)		(Max = 90 min)
Bottle Blank												
Duplicate												
Matrix spike												

a – 24-hour timescale

II. Analytical Procedures

Analytical Batch Sequence Requirements:
The following sequence is required for analysis:
Initial Calibration
Initial Calibration Verification (ICV)
Initial Calibration Blank (ICB)
Interference Check Sample (ICSA & ICSAB) [ICP only]
10 Sample Analyses
Continuing Calibration Verification (CCV)
Continuing Calibration Blank (CCB)
10 Sample Analyses
CCV
CCB
10 Sample Analyses*
CCV*
CCB*
ICS (ICSA & ICSAB) [ICP only]

* This sequence will continue until sample analyses are complete or until one 8-hour shift is complete.

QC Requirements:

QC Sample	Analysis Frequency	Control Limits	Corrective Action[a]
Reagent blank	once per batch	< 25 µg/L Pb <5 µg/L As	Investigate possible sources of target analytes. Mitigate contamination problem before continuing of analysis.
Bottle blank	once per batch (min. 5%)	< 50 µg/L Pb <10 µg/L As	Investigate possible sources of target analytes. Mitigate contamination problem before continuing of analysis.
Blank spike	once per batch (min. 5%)	85-115%	Re-extract and reanalyze sample batch
Duplicate	10% (min. once/day)	± 20% RPD	Re-homongenize, re-extract and reanalyze
Matrix spike	10% (min. once/day)	75-125% recovery	Perform post-digestion spike
Post-digestion spike	If matrix spike is outside control limits	---	---

RPD – Relative percent difference
a – Action required if control limits are not met

Calibration:

Initial calibration requirements:

- ____ Calibration standards were matrix matched.
- ____ Calibration curve correlation coefficient was ≥0.995.

Continuing calibration requirements:

- ____ All ICVs and CCVs were recovered within control limits (90–110%).
- ____ ICVs and CCVs were run in the correct sequence with the correct frequency.

Continuing calibration blank requirements:

- ____ All ICBs and CCBs did not contain Pb or As at levels outside of control limits ($\pm 3\sigma \times$ IDL).
- ____ ICBs and CCBs were run in the correct sequence with the correct frequency.

Interference check sample requirements (ICP only):

- ____ All ICSAs did not contain significant concentrations of Pb or As ($\leq 3\sigma \times$ IDL).
- ____ All ICSABs were recovered within control limits (80–120%).
- ____ ICSs were run in the correct sequence with the correct frequency.

Serial dilution requirements (ICP only):

- ____ A 1:4 dilution was performed on a non-spiked, non-SRM, non-QC sample.
- ____ The RPD was calculated to evaluate for possible interferences.

Date: September 1999 (Rev. # 0) **SOP No. ISSI-VBI70-10**

Title: *In Vitro* Method for Determination of Lead and Arsenic Bioaccessibility.

Total Pages 7

SYNOPSIS: This SOP describes an *in vitro* laboratory procedure to determine the solubility (bioaccessibility) of arsenic and lead in soil and other solid materials under a standardized set of test conditions. This SOP has been adapted from the method developed by the Solubility/Bioavailability Research Consortium (SBRC).

REVIEWS:

DATE	SIGNATURE/TITLE	ACTION
9/10/99	Brenda Lewis /RPM	Approved for use at the VBI70 Site
9/13/99	WS Brattin	

IN VITRO BIOACCESSIBILITY OF LEAD AND ARSENIC IN SOIL

1.0 INTRODUCTION

When a human ingests contaminated soil, the health risk to the person depends on the fraction of the ingested chemical that is absorbed into the body. The fraction of an ingested dose of chemical that is absorbed into the body is referred to as the "bioavailability". For convenience, the bioavailability of a chemical in soil is usually described in comparison to the bioavailability of the pure chemical given in water or food. This ratio is called the "relative bioavailability" (RBA):

$$RBA = \frac{Bioavailability\ of\ chemical\ in\ test\ material}{Bioavailability\ of\ reference\ material}$$

The RBA may differ widely between chemicals and between soils, depending on a number of chemical and physical attributes of each.

The RBA of a chemical in a soil is usually estimated by studies performed using an appropriate animal model. During the period 1989–97, EPA Region VIII developed and applied a juvenile swine model to measure RBA of lead and arsenic in approximately 20 soils/solid materials (Weis and LaVelle 1991; Weis et al. 1994; Casteel et al. 1997a). However, such tests are costly and require special laboratory equipment and technical skills. For this reason, alternative methods for estimating bioavailability are of interest.

Several researchers have developed in vitro tests to measure the fraction of a chemical solubilized from a soil sample under simulated gastrointestinal conditions. This measurement is referred to as "bioaccessibility". Bioaccessibility is thought to be an important determinant of bioavailability, and several groups have sought to compare bioaccessibility determined in the laboratory to bioavailability determined in animal studies. Results obtained to date indicate that in vitro bioaccessability measurements may provide useful information on the in vivo bioavailability for lead and arsenic.

The method described in this SOP represents an in vitro method for measuring the bioaccessability of lead and arsenic in soils and other similar solid materials. The method employed was developed by the Solubility/Bioavailability Research Consortium (SBRC), based on earlier work by Imber (1993), Ruby et al. (1993, 1996), and Medlin (1997).

2.0 SAMPLE PREPARATION

All soil/material samples are prepared by drying (<40 °C) and sieving to <250 μm. The <250-μm size fraction is used because this particle size is representative of that which adheres to children's hands. Samples must be thoroughly mixed prior to use to ensure homogenization before removal of the dose material.

3.0 APPARATUS AND MATERIALS

3.1 Equipment

The main piece of equipment required for this procedure is a Toxicity Characteristic Leaching Procedure (TCLP) extractor motor that has been modified to drive a flywheel. This flywheel in turn drives a Plexiglass block situated inside a temperature-controlled water bath. The Plexiglass block contains ten 5-cm holes with stainless steel screw clamps, each of which is designed to hold a 125-mL wide-mouth high density polyethylene (HDPE) bottle. The water bath must be filled such that the extraction bottles are immersed. Temperature in the water bath is maintained at 37± 2 °C using an immersion circulator heater (for example, Fisher Scientific Model 730. The 125-mL HDPE bottles must have an air-tight screw-cap seal (for example, Fisher Scientific 125-mL wide mouth HDPE Cat. No. 02-893-5C), and care must be taken to ensure that the bottles do not leak during the extraction procedure. Additional equipment for this method includes typical laboratory supplies and reagents, as described in the following sections.

3.2 Standards and Reagents

The leaching procedure for this method uses an aqueous extraction fluid at a pH value of 1.5. The pH-1.5 fluid is prepared as follows:

Prepare 2 L of aqueous extraction fluid using ASTM Type II deionized (DI) water. The buffer is made up in the following manner. To 1.9 L of DI water, add 60.06 g glycine (free base, Sigma Ultra or equivalent). Place the mixture in a water bath at 37 °C until the extraction fluid reaches 37 °C. Standardize the pH meter using temperature compensation at 37 °C or buffers maintained at 37 °C in the water bath. Add concentrated hydrochloric acid (12.1 N, Trace Metal grade) until the solution pH reaches a value of 1.50 ±0.05 (approximately 60 mL). Bring the solution to a final volume of 2 L (0.4 M glycine).

All reagents must be free of lead and arsenic, and the final fluid must be tested to confirm that lead and arsenic concentrations are less than one-fourth the project-required detection limits (PRDLs) of 100 and 20 µg/L, respectively (e.g., less than 25 µg/L lead and 5 µg/L arsenic in the final fluid; see Table 1 in the QAPP).

Cleanliness of all materials used to prepare and/or store the extraction fluid and buffer is essential. All glassware and equipment used to prepare standards and reagents must be properly cleaned, acid washed, and finally, rinsed with deionized water prior to use.

4.0 LEACHING PROCEDURE

Measure 100 ± 0.5 mL of the extraction fluid, using a graduated cylinder, and transfer to a 125-mL wide-mouth HDPE bottle. Add 1.00 ± 0.05 g of test substrate (<250 µm) to the bottle, ensuring that static electricity does not cause soil particles to adhere to the lip or outside threads of the bottle. If necessary, use an antistatic brush to eliminate static electricity prior to adding soil. Record the volume of solution and mass of soil added to the bottle. Hand-tighten each bottle top and shake/invert to ensure that no leakage occurs, and that no soil is caked on the bottom of the bottle.

Place the bottle into the modified TCLP extractor, making sure each bottle is secure and the lid(s) are tightly fastened. Fill the extractor with 125-mL bottles containing test materials or Quality Control samples.

The temperature of the water bath must be 37± 2 °C. Record the temperature of the water bath at the beginning and end of each extraction batch.

Rotate the bottles in the extractor end over end at 30± 2 rpm for 1 hour. Record start time of rotation. When extraction (rotation) is complete, immediately remove bottles, wipe them dry and place them upright on the bench top.

Allow the bottles to stand for about 15-30 minutes to allow the soil or other test material to settle to the bottom of the bottle. Open the bottle and draw extract directly into a disposable 20-cc syringe with a Luer-Lok attachment. Attach a 0.45-µm cellulose acetate disk filter (25 mm diameter) to the syringe, and filter the extract into a clean 15-mL polypropylene centrifuge tube or other appropriate sample vial for analysis. If the total elapsed time between the end of the extraction and the time of sample filtration is greater than 90 minutes, the test must be repeated.

Measure and record the pH of fluid remaining in the extraction bottle. If the fluid pH is not within ± 0.5 pH units of the starting pH, the test must be discarded and the sample reanalyzed as follows:

If the pH has dropped by 0.5 or more pH units, the test will be re-run in an identical fashion. If the second test also results in a decrease in pH of greater than 0.5 s.u., the pH will be recorded, and the extract filtered for analysis. If the pH has increased by 0.5 or more units, the test must be repeated, but the extractor must be stopped at specific intervals and the pH manually adjusted down to pH 1.5 with dropwise addition of HCl (adjustments at 5, 10, 15, and 30 minutes into the extraction, and upon final removal from the water bath [60 min.]). Samples with rising pH values must be run in a separate extraction, and must not be combined with samples being extracted by the standard method (continuous extraction).

Store filtered sample(s) in a refrigerator at 4 °C until they are analyzed. Analysis for lead and arsenic concentrations must occur within 1 week of extraction for each sample.

5.0 QUALITY CONTROL/QUALITY ASSURANCE

Quality Assurance for the extraction procedure will consist of the following quality control samples:

Reagent Blank—extraction fluid analyzed once per batch.

Bottle Blank—extraction fluid only (no added test material) run through the complete procedure at a frequency of 1 in 20 samples.

Blank Spike—extraction fluid spiked at 10 mg/L lead and 1 mg/L arsenic (use traceable 1,000 mg/L lead and arsenic standards in 2 percent nitric acid for making spikes), and run through the complete procedure at a frequency of 1 in 20 samples.

Duplicate Sample—duplicate sample extractions to be performed on 1 in 10 samples.

Matrix Spikes--a subsample of each material used for duplicate analyses will also be used as a matrix spike. The spike will be prepared at 10 mg/L lead and 1 mg/L arsenic (spike concentrations are given for the 100-mL test fluid volume) and run through the extraction procedure (frequency of 1 in 10 samples). Use tractable 1,000 mg/L lead and arsenic standards in 2 percent nitric acid for

making the matrix spikes.

6.0 CHAIN-OF-CUSTODY PROCEDURES

All test materials will be transmitted to the test laboratory under chain-of-custody seal. Once materials are received, the laboratory will maintain and record custody of samples at all times.

7.0 DATA HANDLING AND VERIFICATION

All sample and fluid preparation calculations and operations must be recorded in bound and numbered laboratory notebooks. Each page must be dated and initialed by the person performing any operations. Extraction and filtration times must be recorded, along with pH measurements, adjustments, and buffer preparation. Copies of all laboratory notebook pages must be submitted with the data package.

8.0 REFERENCES

Casteel, S.W., R.P. Cowart, C.P. Weis, G.M. Henningsen, E. Hoffman et al. 1997a. Bioavailability of lead in soil from the Smuggler Mountain site of Aspen, Colorado. Fund. Appl. Toxicol. 36:177–187.

Casteel, S.W., L.D. Brown, M.E. Dunsmore, C.P. Weis, G.M.Henningsen, E. Hoffman, W.J. Brattin, and T.L. Hammon. 1997b. Relative Bioavailability of arsenic in mining waste. U.S. Environmental Protection Agency, Region VIII, Denver, CO.

Imber, B.D. 1993. Development of a physiologically relevant extraction procedure. Prepared for BC Ministry of Environment, Lands and Parks, Environmental Protection Division, Victoria, BC. CB Research International Corporation, Sidney, BC.

Medlin, E.A. 1997. An *in vitro* method for estimating the relative bioavailability of lead in humans. Masters thesis. Department of Geological Sciences, University of Colorado, Boulder.

Ruby, M.W., A. Davis, T.E. Link, R. Schoof, R.L. Chaney, G.B. Freeman, and P. Bergstrom. 1993. Development of an *in vitro* screening test to evaluate the *in vivo* bioaccessibility of ingested mine-waste lead. Environ. Sci. Technol. 27(13):2870–2877.

Ruby, M.W., A. Davis, R. Schoof, S. Eberle, and C.M. Sellstone. 1996. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environ. Sci. Technol. 30(2):422–430.

Weis, C.P., and J.M. LaVelle. 1991. Characteristics to consider when choosing an animal model for the study of lead bioavailability. In: Proceedings of the International Symposium on the Bioavailability and Dietary Uptake of Lead. Sci. Technol. Let. 3:113–119.

Weis, C.P., R.H. Poppenga, B.J. Thacker, and G.M. Henningsen. 1994. Design of phamacokinetic and bioavailability studies of lead in an immature swine model. In: Lead in paint, soil, and dust: health risks, exposure studies, control measures, measurement methods, and quality assurance, ASTM STP 1226, M.E. Beard and S.A. Iske (Eds.). American Society for Testing and Materials, Philadelphia, PA, 19103-1187.

APPENDIX B: CHAIN-OF-CUSTODY RECORDS FOR PAX MATERIAL

Response to Information Request
for the Vasquez Boulevard/I-70 Site, Denver, CO
Received by Martin on 2-22-99

Question 1:
Identify the person(s) answering these Questions on behalf of Respondent.

Answer to Question 1:

Mr. Gary L. Hamar
Lawn & Garden/Specialty Sales Manager
Martin Resources, Inc.
P. O. Box 1450
Plainview, Texas 79073
Telephone (806) 293-2501

Question 2:
For each and every Question contained herein, identify all persons consulted in the preparation of the answer.

Answer to Question 2:

In answering the questions herein, the following people participated in verbal interviews as well as in searching for relevant documents:

Terry Fox, Salt Lake City Plant Operations for Martin Resources, Inc.
Martin Resources, Inc.
580 West 13th South
Salt Lake City, Utah 84115

Garry Ashley, PAX Division Operations Manager for Martin Resources, Inc.
Martin Resources, Inc.
580 West 13th South
Salt Lake City, Utah 84115

Joanne Corona, part-time clerical. Retired in 1997 after 30 years of service to The PAX Company.
Martin Resources, Inc.
580 West 13th South
Salt Lake City, Utah 84115

Rudy Schneider
Martin Resources, Inc.
P. O. Box 1450
Plainview, Texas 79073

Legal counsel was provided by:

James C. Morriss III
Elizabeth A. Webb
Thompson & Knight, P.C.
1200 San Jacinto Center
98 San Jacinto Blvd.
Austin, TX 78701
Telephone (512) 469-6100

Question 3:
For each and every Question contained herein, identify the documents consulted, examined, or referred to in the preparation of the answer or that contain information responsive to the Question and provide accurate copies of all such documents.

Answer to Question 3:

The non-privileged documents used in preparing the answers to the questions and containing information responsive to the questions are enclosed and labeled with the question number to which they respond. The following document is being withheld on the basis of the attorney-client privilege:

Letter dated January 16, 1975, from Donald B. Holbrook of Jones, Waldo, Holbrook & McDonough to W. B. Robins, Utah Cooperative Association with attachment.

Question 4:
Please provide the exact chemical composition of the sample (including active and inert ingredients).

Answer to Question 4:

We were not able to find a printed listing depicting the exact chemical composition of the sample.

Because the sample is believed to have come from a bag of the PAX 3-Year Crabgrass Control product that was out of Pax's custody and control for an unknown period of time, we have no knowledge of whether the sample is a representative sample of the PAX 3-Year Crabgrass

Control product. According to information furnished to Gary Hamar, the sample may have come from a bag of PAX 3-Year Crabgrass Control that was furnished to a school system in Colorado, and then returned in a partially-filled bag to the Pax facility in Salt Lake City, Utah sometime later. We do not know whether the bag's contents were commingled with other substances or whether the bag's contents were contaminated by other sources during the time it was out of Pax's custody and control or after it was returned to Pax. On some date after the partially-filled bag was returned to Pax, a cup of the bag's contents was placed in a brown paper sample bag and the sample bag was labeled. The material in this sample bag is what is being referred to in these answers as the "sample." We also do not know whether the sample has been commingled or contaminated with other substances since it was placed in the sample bag. A picture of the sample bag and a copy of the label on the sample bag are enclosed.

See Document Nos. MR 1A and MR 2A provided herein.

Based upon the literature previously provided to EPA, as well as personal recollections by those identified in Question 2, we believe PAX 3-Year Crabgrass Control contained the following ingredients:

8.25%	Lead Arsenate
25.11%	Arsenous Oxide (Arsenic Trioxide)
(Uncertain of percentage)	Expanded perlite
(Approximately) 20.00 %	Ammonium Sulfate
(Uncertain of percentage)	Silica sand

See Document Nos. MR 1-2; MR 3-4; and MR 5-157 previously provided to EPA.

Question 5:
Please provide the date on which the sample was formulated or manufactured.

Answer to Question 5:

As stated above, the sample may have come from a bag of PAX 3-Year Crabgrass Control product that was furnished to a school system in Colorado and subsequently returned. We do not know when this original bag of product was formulated or manufactured. We also do not know the date the partially-filled bag was returned to the Pax facility in Utah, or when the cup of the bag's contents was placed in the brown paper sample bag. The label on the sample bag has a date of April 30, 1971. The sample was split on March 1, 1999, and the split sample was sent to ISSI Consulting Group on this same date.

See Document No. MR 1A provided herein.

Question 6:
Please provide a complete description, to the degree available, of the transportation history of the sample, including chain of custody information.

Answer to Question 6:
According to information furnished to Gary Hamar, the sample may have come from a bag of PAX 3-Year Crabgrass Control that was furnished to a school system in Colorado, and then returned in a partially-filled bag to the Pax facility in Salt Lake City, Utah sometime later. We do not know the name of the school system that returned the partially-filled bag, the persons who handled the bag while it was at the school system, or how or where the school system maintained, used, or stored the bag before returning it to Pax.

On some date after the partially-filled bag was returned to Pax, a cup of the bag's contents was placed in a brown paper sample bag and the sample bag was labeled. We do not know who handled the partially-filled bag after it was returned to Pax, or the persons who placed the sample in the sample bag. The sample bag was stored at the Salt Lake City facility until it was given by Terry Fox to Gary Hamar on December 16, 1998. We do not know all of the people who handled the sample while it was stored in Salt Lake City.

As stated above, on December 16, 1998, Terry Fox at the Salt Lake City facility gave the sample to Gary Hamar. Mr. Hamar took the sample to Martin's facility in Plainview, Texas.

The sample was split on March 1, 1999, and the split sample was sent to ISSI Consulting Group by FEDEX on this same date.

Question 7:
Please describe specific information about the storage container or containers (e.g., jar, can, bag) and the type of material which the container(s) is made of (e.g., glass, metal, plastic, fabric/nylon).

Answer to Question 7:

We do not know how the school system stored the original bag of product that was furnished to it, nor do we know how the partially-filled bag was stored by Pax after it was returned by the school system to Pax's Utah facility. On some date after the partially-filled bag was returned, a cup of the bag's contents was placed in a brown paper sample bag. A picture of this sample bag is enclosed. Except for when the sample was split on March 1, 1999, we do not know whether the sample was ever removed from the brown paper sample bag. When the sample was split on March 1, 1999, the split sample was taken from the brown paper sample bag and was placed in the sample container provided by EPA.

See Document No. MR 2A provided herein.

Question 8:
Please describe whether special procedures were used to maintain the sample, such as inert conditions to reduce oxidation.

Answer to Question 8:

We do not know how or where the school system maintained, used, or stored the original bag of product that was furnished to it, nor do we know how the partially-filled bag was stored by Pax after it was returned to Pax's Salt Lake City, Utah, facility. The bag may have been stored in a warehouse without temperature control. As discussed above, on some date after the partially-filled bag was returned, a cup of the bag's contents was placed in a brown paper sample bag. This sample was then stored at the Salt Lake City facility. There were no special procedures for storage of the sample at Salt Lake City. After the sample was moved to the Plainview facility, no special procedures were used for storage of the sample. The sample was stored in an unlocked closet in Mr. Hamar's office.

Question 9:
Please describe conditions in the area in which the sample was stored, including, but not limited to, temperature, humidity and lighting.

Answer to Question 9:

We do not know how or where the school system maintained, used, or stored the original bag of product that was furnished to it, nor do we know how the partially-filled bag was stored by Pax after it was returned to Pax's Utah facility. The bag may have been stored in a warehouse without temperature control. After a cup of the bag's contents was placed in the sample bag, the sample bag was stored at the Utah facility. We do not know all of the storage conditions for the sample for the entire time it was stored at the Utah facility. We do know that for some period of time, the sample bag was stored in an unlocked cabinet in the "lab area." This cabinet was dark except when the cabinet door was open. The lab area was not air conditioned and, therefore, the temperature in the area in the summer would be close to the outside temperature which could sometimes be as high as 95°F to 100°F. The lab area did have a heater and winter temperatures in the area would be approximately 70°F.

After the sample was moved to the Plainview facility, the sample was stored in an unlocked closet in Mr. Hamar's office. The storage conditions in the closet were normal office temperature and environment. The closet doors are louvered to allow for air circulation, thus the conditions in the closet are substantially the same as in the office with the exception of the amount of light. The only time there is light in the closet is when the closet doors are open.

Question 10:
Please describe the security or chain of custody procedures used for samples in the storage area.

Answer to Question 10:

Salt Lake City Facility

Fertilizer samples are stored in Salt Lake City in an unlocked cabinet in the "lab area." There are numerous personnel placing samples into the cabinet periodically. Sometime later, usually six months to one year after storage, the samples are placed into the plant food materials for distribution to our customers. In this way, we rotate the samples and keep from overloading our storage cabinet.

Plainview Facility

While the sample was stored in the closet in Mr. Hamar's office, no special security procedures were employed. However, most people could not have located the sample without upheaval of the closet's contents. Such upheaval was never observed.

Question 11:

Please provide the name of the source for the lead arsenate used in PAX 3-Year Crabgrass Control.

Answer to Question 11:

According to information furnished to Gary Hamar, the only remembered shipments of lead arsenate used in PAX 3-Year Crabgrass Control were from Chevron and Woolfolk Chemical.

52115 09701 Austin 114024.1

NOTARIZED CERTIFICATE

STATE OF TEXAS §
§
COUNTY OF HALE §

BEFORE ME, the undersigned authority, on this day personally appeared Gary L. Hamar, who, after having been duly sworn, stated that the above and foregoing answers are accurate, complete, and true and correct.

Gary L. Hamar
(Signature)

SWORN TO AND SUBSCRIBED BEFORE ME by the said Gary L. Hamar on this the 11th day of March, 1999, to certify which, witness my hand and seal of office.

Notary Public, in and for the State of Texas

[SEAL]

QUESTIONS 4 AND 5

PAX COMPANY
580 West 1300 South
Salt Lake City, Utah 84115

Date April 30 1971

Analysis Requested: 4 N 0 P_2O_5 0 K_2O ___ Other

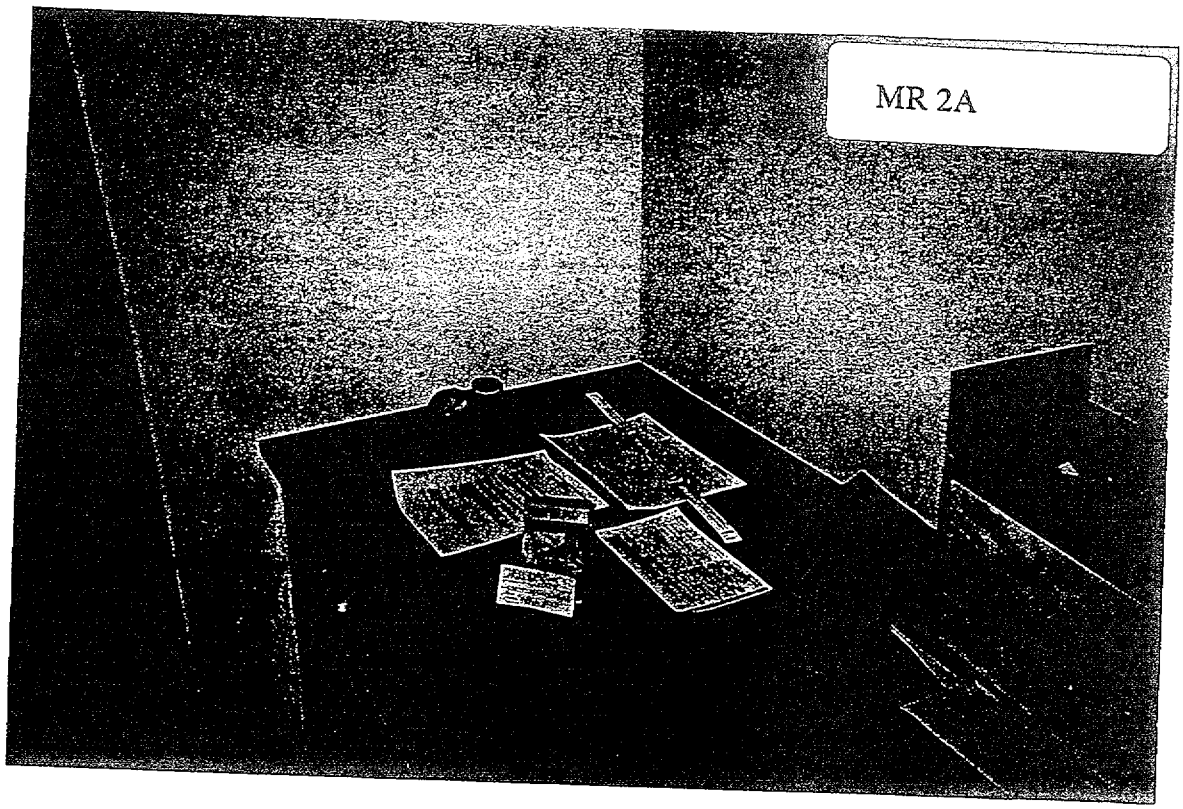
Sample Identification:
Product 3yr Pax Crabgrass

Grade

Sample # Batch 4

Batch Code 4-30-71

QUESTIONS 4 AND 7


MR 2A

APPENDIX C: METALS CORRELATION ANALYSIS

ISSI Consulting Group
999 18th Street, Suite 1450
Denver, CO 80202
ph 303.292.4142 • fax 303.292.4926

U.S. SBA 8(a) certified
postmaster@issiinc.com
www.issiinc.com

MEMORANDUM

To: Chris Weis & Bonnie Lavelle

From: Mary Goldade

Date: September 8, 1999

Project Name: Vasquez Boulevard & I-70

RE: Metals Correlation in Site Soils

cc: Project Files

Purpose

The VBI70 Pilot-Scale Soil Characterization Study is intended to investigate a series of chemical and physical attributes of contaminated site soils that may help identify the source of the contamination. One possible type of attribute is the ratio of arsenic concentration to the concentration other metals in the soil. That is, if arsenic and a set of other metals are all derived from the same source, then the ratios of those metals may be helpful as a "fingerprint" of the source material. Thus, the purpose of this study was to utilize existing data from site soils to investigate which metals, if any, were correlated with the occurrence of arsenic.

Existing Data

To date, USEPA Region 8 has completed three major studies at the VBI70 site: Phase I Field Sampling, Phase II Field Sampling and Risk-Based Sampling Programs. Although the primary objective of these investigations was to determine the nature and extent of arsenic and lead levels in soils at the VBI70 site, the full list of 23 target analyte list (TAL) metals was measured for 54 different samples. Most of these samples (44 out of the total 54) were samples that were selected for confirmation analysis by inductively coupled plasma (ICP) instrumentation as part of the Phase I sampling program. For these samples, the bulk fraction (sieved to < 2 mm) were analyzed. The remaining samples (N=10) were derived from the Risk-Based Sampling program (USEPA 1998b, 1999) and were analyzed using ICP-mass spectrometry (ICP-MS). The fine fraction (sieved to < 250 μm) was tested for this subset of soils. These samples included two samples randomly chosen from each of 5 impacted residences that were sampled as part of the Risk-Based Sampling program.

Summary of Results

Table 1 shows the Pearson Correlation Coefficient between each of the metals in the set of 54 soil samples analyzed. In brief, four metals appear to modestly correlate ($r > 0.5$) with arsenic. These are: antimony, cadmium, lead and mercury.

Descriptive statistics were also determined for this data set and are provided in Table 2. As seen, the mean arsenic

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Project No.: 96290-ARA-01
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Requisition No.: 9.5770.0175
EPA IAG No.: DW47953681

concentration for the entire dataset (N = 54) is about 540 ppm. In contrast, the average arsenic levels found in the 5 impacted soils (Risk-Based Sampling program) (N = 10) is about 2600 ppm. Due to the significant difference in arsenic levels between the two datasets, a second Pearson correlation analysis was performed on the impacted soils only. This was done to determine if a stronger correlation was observed when higher arsenic levels are present in soil. The results of this analysis is presented in Table 3. As seen, 7 metals appear to modestly correlate with arsenic-bearing soils ($r > 0.5$). These are: antimony, cadmium, lead, mercury, selenium, thallium and calcium.

Conclusion

There is a moderate correlation between the concentration of arsenic and the concentration of seven other metals (antimony, cadmium, lead, mercury, selenium, thallium and calcium) in site soils. Therefore, these seven metals will be analyzed (along with arsenic) in the Pilot-Scale Soil Characterization Study in order to provide data that can be used to test whether the ratios of arsenic to other metals are diagnostic of the source material.

References

USEPA. 1998a. Final Sampling Activities Report for North Denver Residential Soils - Phase I. Prepared by URS Operating Services. June 1998.

USEPA. 1998b. Project Plan for the Vasquez Boulevard and I-70 Residential Risk-Based Sampling Stage I Investigation. Prepared by ISSI Consulting Group, Inc. August 1998.

USEPA. 1999. Draft Report for the Vasquez Boulevard and I-70 Site Residential Risk-Based Sampling Stage I Investigation. Prepared by ISSI Consulting Group, Inc. April 1999.

Attachments

Table 1 - Metals Correlation Results

	ALUMINUM	*ANTIMONY*	*ARSENIC*	*BARIUM*	*BERYLLIUM*	*CADMIUM*	*CHROMIUM*	*COBALT*	*COPPER*	*LEAD*	*MANGANESE*
ALUMINUM	1										
ANTIMONY	0.027610059	1									
ARSENIC	0.042555868	0.98083384	1								
BARIUM	0.434297779	-0.042367	-0.055029	1							
BERYLLIUM	0.83716386	0.25124372	0.290808	0.52208189	1						
CADMIUM	0.52472027	0.51955521	0.531065	0.37179473	0.70697037	1					
CHROMIUM	0.430519171	0.11829879	0.131625	0.37594837	0.41758125	0.540894503	1				
COBALT	0.682570245	-0.01314557	0.013572	0.15507574	0.61760817	0.364463426	0.07308356	1			
COPPER	0.281731582	-0.02904	-0.040035	0.65093373	0.25691152	0.170484547	0.45937246	-0.382621	1		
LEAD	0.252630922	0.56429102	0.5722	0.57760653	0.47792094	0.66040072	0.35909242	0.136302	0.31854	1	
MANGANESE	0.6752984	-0.11567845	-0.132959	0.58003011	0.62527003	0.47823085	0.34105327	0.610231	0.155973	0.2821238	1
MERCURY	0.03694003	0.87082914	0.91322	0.00851013	0.31870887	0.501265522	0.10882682	0.073093	-0.053134	0.5276762	-0.082089367
NICKEL	0.416483956	0.00117442	-0.005105	0.72935875	0.39304694	0.283619305	0.52735461	-0.229928	0.981137	0.3888557	0.276874756
SELENIUM	-0.0752124	-0.25356618	-0.355837	0.13515438	-0.37084689	-0.31402808	-0.12474759	-0.118206	0.062927	-0.235749	0.149454239
SILVER	0.310104838	-0.09858463	-0.097208	0.41653013	0.4240267	0.252678197	0.39601613	0.501235	-0.088766	0.2183093	0.619850819
THALLIUM	0.07481234	-0.39808858	-0.491278	0.15103914	-0.22112968	-0.29074049	-0.09195715	0.136123	-0.02696	-0.336399	0.252904748
VANADIUM	0.803984949	-0.13160982	-0.156254	0.46353865	0.53470664	0.275785081	0.27545048	0.56152	0.247197	0.0884867	0.649424955
ZINC	0.286096276	0.123933	0.134673	0.55307854	0.32145379	0.331430826	0.33987085	-0.016151	0.584496	0.4273876	0.353391677
CALCIUM	0.058029008	0.06416555	0.051505	0.24489636	0.12933622	0.099591913	0.10588608	-0.150929	0.297192	0.1458468	0.000745824
IRON	0.872899162	0.11107711	0.144191	0.58609753	0.83937863	0.561177959	0.53426407	0.506679	0.492064	0.407625	0.617623769
MAGNESIUM	0.923282626	0.19387143	0.231645	0.41520665	0.85386845	0.633499805	0.4663983	0.713865	0.226004	0.3781056	0.622631851
POTASSIUM	0.802226543	-0.08443031	-0.067826	0.1620827	0.59296541	0.239765977	0.13165127	0.672104	0.028375	-0.093637	0.489652933
SODIUM	-0.06488756	0.16857647	0.25326	-0.1103383	0.14388598	0.253774922	0.12341434	-0.037778	-0.048224	0.1709871	-0.169896006

Table 1 - Metals Correlation Results

	MERCURY	*NICKEL*	*SELENIUM*	*SILVER*	*THALLIUM*	*VANADIUM*	*ZINC*	*CALCIUM*	*IRON*	*MAGNESIUM*	*POTASSIUM*	*SODIUM*
ALUMINUM												
ANTIMONY												
ARSENIC												
BARIUM												
BERYLLIUM												
CADMIUM												
CHROMIUM												
COBALT												
COPPER												
LEAD												
MANGANESE												
MERCURY	1											
NICKEL	-0.0158079	1										
SELENIUM	-0.4002144	0.048731	1									
SILVER	-0.0238268	0.018856	0.02198404	1								
THALLIUM	-0.5073221	-0.004282	0.89310989	0.129187	1							
VANADIUM	-0.1383174	0.369113	0.39730171	0.324049	0.52674851	1						
ZINC	0.30637974	0.607906	-0.083619	0.102847	-0.14701477	0.17917839	1					
CALCIUM	0.08412966	0.296971	0.07824081	-0.054431	-0.01193429	0.0964676	0.217696	1				
IRON	0.16398582	0.617724	-0.26991521	0.377222	-0.13143505	0.65679825	0.467475	0.184249	1			
MAGNESIUM	0.2261872	0.375333	-0.22333058	0.33612	-0.05780208	0.69735234	0.310519	0.087986	0.8862408	1		
POTASSIUM	-0.0356016	0.125706	-0.04969375	0.135699	0.16358407	0.62552548	0.057585	-0.107791	0.6406525	0.714517137	1	
SODIUM	0.40165091	-0.055972	-0.64396173	-0.009482	-0.58434931	-0.29646197	0.279164	-0.044645	0.0835365	0.045910412	-0.17872809	1

TABLE 2 SUMMARY STATISTICS FOR SOIL SAMPLES

All Data (Phase I and Risk-Based Sampling)

Analyte	N	Summary Statistics		
		Min	Max	Mean
ALUMINUM	54	4900	15000	8761
ANTIMONY	54	2.2	54	6.8
ARSENIC	54	5	9940	543
BARIUM	54	91	1000	251
BERYLLIUM	54	0.3	1.1	0.7
CADMIUM	54	0.9	19	5.9
CHROMIUM	54	7.2	99	22
COBALT	54	1.0	7.0	4.6
COPPER (a)	53	12	71	37
LEAD	54	36	3550	712
MANGANESE	54	160	560	323
MERCURY	54	0.1	11	1.0
NICKEL	54	5.9	96	11
SELENIUM	54	0.3	10	9
SILVER	54	0.3	3	0.7
THALLIUM	54	0.2	19	11
VANADIUM	54	13	42	21
ZINC	54	84	3680	499
CALCIUM	54	1900	41000	6757
IRON	54	7900	26000	13405
MAGNESIUM	54	1400	4100	2400
POTASSIUM	54	1400	4100	2350
SODIUM	54	300	440	304

a. Excludes one value (14,000 ppm) that is considered anomalous

Risk-Based Sampling Only

Analyte	N	Summary Statistics		
		Min	Max	Mean
ALUMINUM	10	6650	12100	9177
ANTIMONY	10	2.2	54	15
ARSENIC	10	127	9940	2585
BARIUM	10	121	339	207
BERYLLIUM	10	0.6	1.1	0.8
CADMIUM	10	1.6	19	10
CHROMIUM	10	8.6	56	27
COBALT	10	3.5	6.8	4.9
COPPER (a)	10	20	71	41
LEAD	10	171	3550	1246
MANGANESE	10	170	396	294
MERCURY	10	0.2	11	3.5
NICKEL	10	6.7	12	10
SELENIUM	10	0.3	5.2	1.9
SILVER	10	0.3	1.1	0.7
THALLIUM	10	0.2	0.7	0.5
VANADIUM	10	13	21	16
ZINC	10	86	3680	684
CALCIUM	10	2150	9960	5983
IRON	10	12400	19400	15790
MAGNESIUM	10	2020	3390	2810
POTASSIUM	10	1650	4320	2393
SODIUM	10	100	648	451

Table 3 - Metals Correlation Results
Impacted Residences Only

	ALUMINUM	*ANTIMONY*	*ARSENIC*	*BARIUM*	*BERYLLIUM*	*CADMIUM*	*CHROMIUM*	*COBALT*	*COPPER*	*LEAD*	*MANGANESE*
ALUMINUM	1										
ANTIMONY	-0.05961154	1									
ARSENIC	-0.035351446	0.988488285	1								
BARIUM	0.780083772	0.084599497	0.118198576	1							
BERYLLIUM	0.869141352	0.208510678	0.256669013	0.791271329	1						
CADMIUM	0.23955281	0.701240935	0.69636393	0.451901909	0.452233481	1					
CHROMIUM	-0.144956002	0.148723505	0.13122963	-0.248751071	-0.200228407	0.422406236	1				
COBALT	0.961040266	-0.22652833	-0.197898325	0.737926002	0.726070098	0.070823126	-0.179372641	1			
COPPER	0.45973563	0.193440309	0.211650307	0.760153009	0.536521182	0.621958768	0.077433832	0.426274547	1		
LEAD	0.25247055	0.816993367	0.821852803	0.497954076	0.482886238	0.908531735	0.333131993	0.07708903	0.564260582	1	
MANGANESE	0.87862849	-0.147406802	-0.15225999	0.613373053	0.618359687	0.312339169	0.191638931	0.887602291	0.458668317	0.204333572	1
MERCURY	-0.028848339	0.870594473	0.911081723	0.076938728	0.196762534	0.550680425	0.00399749	-0.119073913	0.17046075	0.645277485	-0.113920631
NICKEL	0.781103528	0.375189007	0.392991689	0.70991969	0.81038037	0.749744261	0.295733795	0.661494692	0.665740833	0.699248204	0.766961137
SELENIUM	-0.00421004	0.955072441	0.969024055	0.154927202	0.238039403	0.751225663	0.176469034	-0.144087721	0.244709272	0.830160305	-0.0449453
SILVER	0.418544842	-0.346725481	-0.358864315	0.053042471	0.229085067	-0.057810442	0.427719513	0.409254547	0.107189209	-0.065016438	0.577803886
THALLIUM	0.101312509	0.738801402	0.738809933	0.245168596	0.319015472	0.93179052	0.510330332	-0.044275615	0.565328416	0.824370428	0.195502833
VANADIUM	0.494414849	0.26891374	0.368885578	0.403776953	0.728200849	0.330558876	-0.204313209	0.404756097	0.403422722	0.289046343	0.260289317
ZINC	0.157612679	0.107600516	0.120452302	0.064956891	-0.038011651	0.050983254	-0.058493614	0.232957191	-0.142653821	0.060980129	0.303977521
CALCIUM	0.499803478	0.516067926	0.559835447	0.75960771	0.585256124	0.754838445	0.11417413	0.430354111	0.707962798	0.821502974	0.468236902
IRON	0.711673356	-0.077684948	-0.080525833	0.44500065	0.454880944	-0.13040736	-0.134823532	0.773363175	0.326049743	0.036250296	0.624109529
MAGNESIUM	0.836509625	0.261514506	0.303536179	0.687524343	0.759561916	0.481062016	0.244035558	0.778790541	0.515504729	0.585009242	0.780711217
POTASSIUM	0.482591077	-0.249097573	-0.220423261	0.24649964	0.2589779	-0.478359719	-0.548087516	0.616091339	0.039990855	-0.36681481	0.288835832
SODIUM	-0.561699248	-0.194167633	-0.169027168	-0.314582339	-0.496496635	-0.050630604	0.091938191	-0.492449606	-0.050311252	-0.188541265	-0.34902629

Table 3 - Metals Correlation Results
Impacted Residences Only

MERCURY	NICKEL	SELENIUM	SILVER	THALLIUM	VANADIUM	ZINC	CALCIUM	IRON	MAGNESIUM	POTASSIUM	SODIUM
1											
0.286277887	1										
0.191225865	0.421664181	1									
-0.349949384	0.272739537	-0.3082716	1								
0.607085916	0.685820762	0.75505316	-0.121814916	1							
0.469940201	0.553534137	0.341929039	-0.04648461	0.402751558	1						
0.398292901	0.013912255	0.322815395	0.11961989	-0.093914244	-0.073564855	1					
0.576940717	0.715874065	0.6622501	0.031014417	0.593390972	0.386980107	0.399699139	1				
-0.031769922	0.422485847	-0.10714314	0.481142149	-0.121351702	0.214397042	0.108315563	0.239532298	1			
0.278476531	0.187258801511	0.339586981	0.444981277	0.399542753	0.471780536	0.223839365	0.726184859	0.670517227	1		
-0.058096829	0.060403299	-0.27593891	-0.015882665	-0.382158339	0.325566568	0.033312982	-0.096353868	0.753359276	0.265073738	1	
0.040424517	-0.487289733	-0.02186012	-0.010572393	-0.105511245	-0.227792087	0.362476237	-0.008154459	-0.579540699	-0.491533233	-0.522433042	1